STUDIES ON THE DEGRADATION OF STARCH

by

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PREFACE

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SUMMARY

SUMMARY

Differential thermal analysis was carried out on starches from several different botanical sources, and of their component amylose and amylopectin, and the thermograms compared. It was found that the presence of "inert" materials such as alumina profoundly affected the thermograms of starch. All analyses had therefore to be carried out without the addition of any "inert" material. Factors affecting the starch thermograms, such as the physical structure of the granule and percentage amylose content, were investigated. It was noted that thermograms similar to those of starch were obtained from the oligomer series G_1 to G_7, where thermal stability of these oligomers was found to increase with increase in their chainlength.

The pyrolysis over a temperature range of 220 to 300°C of the oligomer series, G_1 to G_7, β-Schardinger dextrin, potato starch and its components amylose and amylopectin, retrograded amylose, and dextran was studied. The amounts of the various products from each substance at the different temperatures were compared.

Rates of production of the major volatiles, i.e. carbon monoxide, carbon dioxide and water, from each of the compounds were measured at the various temperatures, and activation energies for the degradation calculated. The natures of the residues and 'syrup' fractions were investigated. The influence on the thermal breakdown of temperature, molecular size and type of glycosidic linkage were studied. The significance of these results is discussed and possible modes of degradation are suggested.

INTRODUCTION

INTRODUCTION

When starch is heated a large number of different reactions occur, producing a complicated breakdown pattern. The extent of modification, or breakdown, of the starch depends on the temperature and time involved, but generally includes both physical and structural changes in the solid along with the production of volatile products.

An outline of the chemistry of starch is given in Section 1, and the literature on the changes brought about in it by the application of heat is reviewed in Sections 2 and 4, Section 2 being concerned with evidence regarding the physical and external changes, while Section 4 describes work carried out to study the chemical effects.

The small amount of work which has been reported in the literature has not been sufficient to determine the mode of degradation of starch on either dextrinization or pyrolysis. Rather, it has demonstrated that it is an exceedingly complex process. This thesis has attempted to gain some information on the breakdown of starch, by studying the thermal degradation of "model" compounds of starch, and of polysaccharides related to it, as well as of starch itself.

Section 3 describes a study of a number of starches from different botanical sources, of their components, and of the maltodextrins by differential thermal analysis. The results of pyrolysis studies carried out *in vacuo* on starch and related compounds are presented in Section 5.

SECTION 1 : THE CHEMISTRY OF STARCH

THE CHEMISTRY OF STARCH

Starch can be found in most land plants and is the most abundant and most important of their reserve polysaccharides. It is also the chief source of carbohydrate in the human diet. Basically a polymer of D-glucopyranose units, it may also contain small amounts of phosphorus, which is present in the form of phosphate-ester attached to the C_6 position of some of the glucose residues (Posternak, 1935). Trace amounts of silica, other mineral matter, fatty acids, protein and lipids may also be present (Whelan, 1958), but it is unlikely that these form part of the actual starch material and they probably occur as contaminants.

The heterogeneity of starch was recognised in the 1920's (for a review, see Schoch, 1945) but the first quantitative separation of starch into two fractions with quite distinct properties was not carried out until 1942 when Schoch selectively precipitated one fraction with butanol. The precipitated fraction is now known as amylose, and the remaining, non-precipitated, fraction is called amylopectin. However, the suggestion has to be considered that starch is one giant, homogeneous molecule, and that the apparent separation of the two components is a result of degradation. No experimental results have yet been put forward to support this contention, but proof would be difficult to obtain as it would involve dispersing the granular structure without degradation. It should also be noted that indirect evidence has been obtained of a third fraction, intermediate in properties between amylose and amylopectin (Lansky, Kooi and Schoch, 1949; Banks and Greenwood, 1959 and 1967).

The proportions of amylose and amylopectin in a starch depend on the botanical source from which the starch has been isolated. The amylose-content can be less than 1% (as in waxy, or glutinous, starch such as maize) or approach 80% (as in amylomaize starch). Generally, however, about 20% of a

starch consists of amylose.

Early work was carried out on incompletely separated components and the main structural features were actually established during this time. Some of

Table 1.1

Property	Amylose	Amylopectin
Molecular configuration	Essentially linear	Branched molecule
Molecular weight	ca. 10^6	ca. 10^8
X-ray diffraction	Crystalline	Amorphous or weakly crystalline
Complex formation	Readily forms complexes with polar substances	Very limited complex formation with polar substances
Iodine colouration	Intense blue	Purple-brown
Solubility in aqueous solution	Unstable, tends to retrograde	Stable
β-amylolysis limit	ca. 70 - 80% conversion into maltose	ca. 55% conversion into maltose
Action of β-amylase + Z-enzyme	Complete hydrolysis	High molecular weight dextrins

the characteristic properties of amylose and amylopectin are shown in Table 1.1 and each component is dealt with in more detail below.

Amylopectin

Using methylation and hydrolysis methods, Meyer, Wertheim and Bernfeld (1940) deduced that amylopectin, which gave 1 terminal end-group per 27 glucose

units, i.e. a "chainlength" of 27, in a sample of degree of polymerisation (DP) greater than 1300, must be highly branched. Later studies, using methylation and periodate oxidation (Bobbit, 1956; Greenwood, 1956; Whelan, 1958), and, more recently, enzymic characterization (Adkins, Banks and Greenwood, 1966), while essentially substantiating the structure, have found, for amylopectin from different varieties of starch, values between 17 and 26 for the number of D-glucose residues per unit chain.

In contrast to the linear α-1→4-linkage, it was indicated that the linkage at the branch-point in amylopectin was 1→6 by methylation and hydrolysis (Barker, Hirst and Young, 1941), and by its successful disruption by α-1→6-glucosidase (Meyer and Bernfeld, 1940a). The presence of this branch-point was proved by the isolation of isomaltose (6-α-D-glucopyranosyl-D-glucose) from the hydrolysis of amylopectin by enzymes (Montgomery, Weakley and Hilbert, 1949), and by acid (Wolfrom, Tyree, Galkowski and O'Neill, 1951). Panose (4-α-isomaltopyranosyl-D-glucose) was also isolated from the acid hydrolysate (Thompson and Wolfrom, 1951). The fact that no D-glucose remains after periodate oxidation indicates that there are no branch-points at C_2 or C_3 (Gibbons and Boissonnas, 1950).

Three possible branched structures, which have been postulated for amylopectin, are shown in Figure 1.1. All three contain different arrangements of the same basic, linear, unit chains. The laminated structure (A) was put forward by Haworth, Hirst and Isherwood (1937; see also Halsall, Hirst, Hough and Jones, 1949) as a representation of a structure which was in accordance with the small change in the number of non-reducing end-groups with large changes in molecular weight. Staudinger and Husemann (1937) suggested the comb-like structure (B) after comparing the viscosities of solutions of starch and cellulose having similar molecular weights. Enzymes were used by

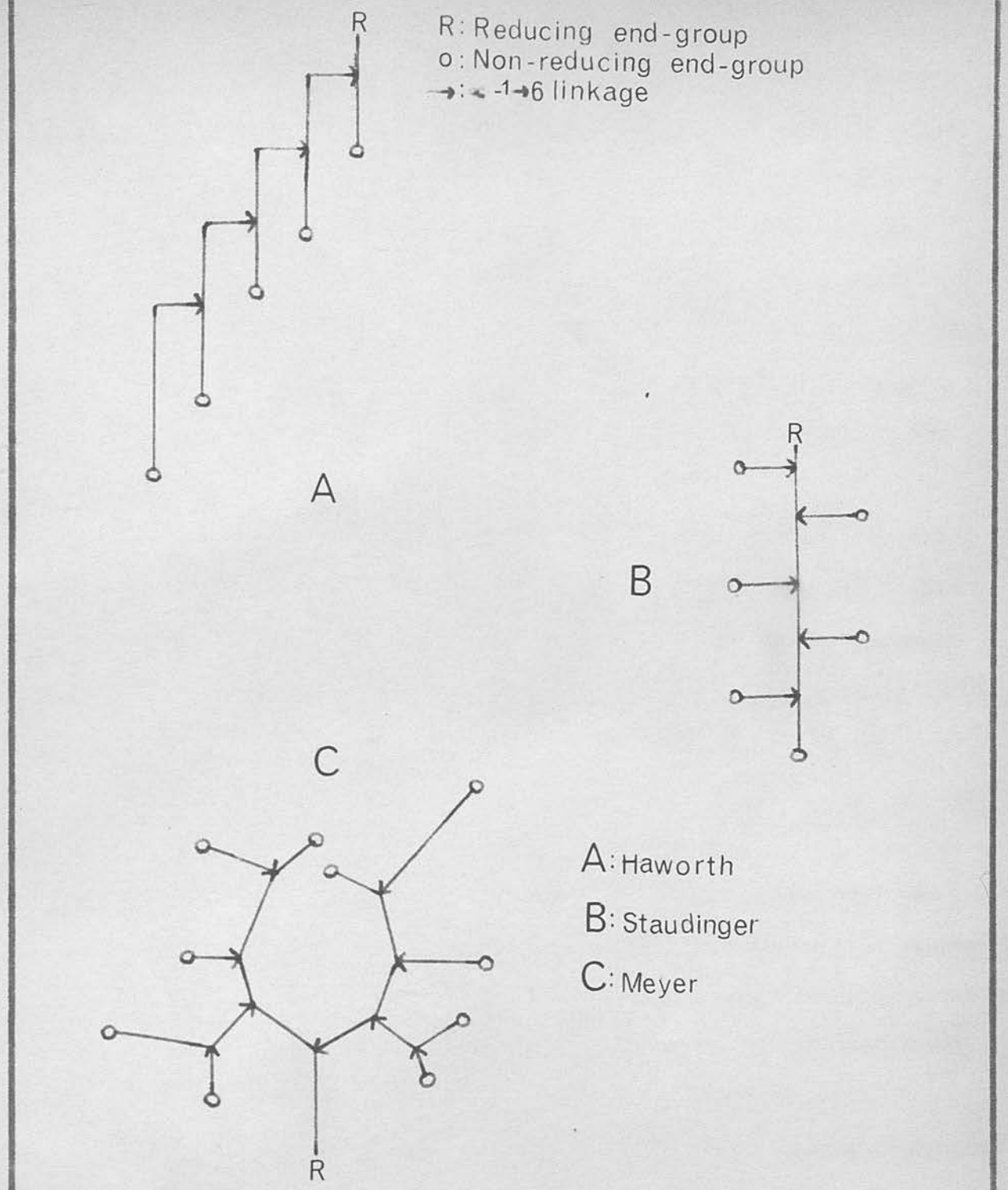


FIG. 1.1 Possible Amylopectin Structures

Meyer and Bernfeld (1940a) to derive the arborescent formula (C). They found that treatment of amylopectin with β-amylase, which attacks from the non-reducing end of the chain, would give only about 50% maltose. When the remaining "β-limit dextrin" was treated with α-1→6-glucosidase —— an enzyme specific for α-1→6 bonds —— about 7% of glucose was detected. β-amylase could then release more maltose from the amylopectin. Results from this successive use of β-amylase and α-1→6-glucosidase led Meyer and Bernfeld to discount formulae (A) and (B) in favour of structure (C). The last structure has been supported by later enzymic studies using β-amylase and R-enzyme (Peat, Whelan and Thomas, 1952) and phosphorylase and amylo-1→6-glucosidase (Larner, Illingworth, Cori and Cori, 1952).

Measurements of the molecular weight of amylopectin, generally by the techniques of lightscattering or osmometry, have shown it to be one of the largest molecules found in Nature (Greenwood, 1960). The actual molecular weight of the amylopectin varies with the plant source but is generally of the order of 10^6.

Amylose

Early studies by means of methylation and hydrolysis showed that the number of end-groups in amylose was about ten times less than that in amylopectin. These end-group assays, in conjunction with molecular weight determinations by osmotic pressure, indicated the essentially linear nature of amylose (Meyer, Wertheim and Bernfeld, 1940 and 1941; Hassid and McCready, 1943).

When early workers found that β-amylase converted amylose completely into maltose (Meyer and Bernfeld, 1940a) this was taken as further proof of the linearity of the molecule. More recently, however, it has been found that pure β-amylase achieves only about 75% conversion of amylose into maltose (Peat,

Pirt and Whelan, 1952), and that the presence of another enzyme, Z-enzyme, is necessary for 100% conversion of whole amylose samples. By careful aqueous leaching of the starch granules, a low molecular weight amylose can be obtained which is completely hydrolyzed by the enzyme (Cowie and Greenwood, 1957a).

It is possible that the action of β-amylase is obstructed by some modification introduced during isolation of the amylose (Bottle, Gilbert, Greenwood and Saad, 1953). That oxidation of the amylose can cause such a barrier was shown by Banks, Greenwood and Thompson (1959). Similarly, Posternak (1951) has shown that ester-phosphate groups obstruct the action of β-amylase. This idea was supported by Banks and Greenwood (1967), who also showed that Z-enzyme is a weak α-amylase. This being the case, any, or all, of the above suggestions may contribute to the stopping of the β-amylase action.

As the α-1→4-linkage can exist in various conformations the amylose molecule is capable of attaining different shapes in solution. In concentrated solutions, the amylose can form linear chains which may align themselves to form bundles of molecules and, eventually, visible micelles, held together by hydrogen bonding. This precipitation, called "retrogradation", of amylose is not easily reversible. Retrogradation depends on the pH, on the concentration of the amylose solution and the type of amylose and, perhaps most importantly, on the molecular weight of the amylose (Lansky, Kooi and Schoch, 1949).

The determination of physical properties of free amylose in aqueous solution is complicated by this phenomenon of retrogradation. Many measurements, such as molecular weight determinations, are therefore carried out on derivatives. The acetate is normally used since the acetylation procedure using pyridine as a catalyst causes little degradation and gives high yields (Greenwood and Robertson, 1954). Viscosity, sedimentation and osmotic pressure measurements

on the acetate have shown amylose to have a degree of polymerisation (DP) of about 4,000 (Cowie and Greenwood, 1957a). However, amylose consists of a continuous series of homologous linear polymers rather than a limited number of discrete compounds (Lansky, Kooi and Schoch, 1949).

The Starch Granule

The size and shape of the starch granule is characteristic of both the species of plant and the part of the plant from which it is derived. The size of granules from different sources ranges from 1μ to 150μ, and even in granules from the same source there is a decided variation in size.

Starch granules are strongly birefringent and exhibit, in polarized light, two dark lines which intersect at the hilum. The granule appears to be deposited in layers around the hilum, and striations from these layers can be clearly seen in some starches . An example of a photomicrograph showing clearly these striations in starch granules from the potato berry is given by Greenwood and MacKenzie (1963).

Nothing definite is known of the way in which the amylose and amylopectin components actually pack together in the granule. Meyer and Bernfeld (1940b) have suggested that the birefringent properties were caused by the presence of spherulites, which consist of small crystalline regions held together by secondary valency forces. These crystalline regions were thought to be composed of parts of the amylopectin molecules, one amylopectin molecule being part of several crystallites, with amorphous portions in between. (Meyer and Menzi, 1953). Amylose, when present, could then form mixed crystals with the amylopectin.

The molecular orientation present in starch is also demonstrated by the X-ray diffraction patterns. Although there are many experimental difficulties

to be overcome before the configuration of the starch molecules in the granule can be determined, some information has already been obtained. Starch can be classified into two types, those which give an "A"-type pattern (cereal starches) and those which give a "B"-type pattern (tuber starches) (Katz and van Itallie, 1930; Katz and Derkson, 1933). This is not a rigid classification, however, as some starches exhibit intermediate "C"-type patterns, and all starches give an "A"-type pattern if retrograded above 50°C, and a "B"-type pattern when retrograded at low temperatures.

A "V"-type pattern may also be obtained when starch is precipitated from solution by alcohol. Bear (1942) has suggested that, in this modification, a helical configuration of the molecules is likely.

Water of crystallization appears to be important since drying of the grains produces an irreversible amorphous X-ray pattern, although birefringence remains (Brimhall, 1944).

Although separated amylopectin, unlike amylose, generally gives an amorphous pattern, granular amylopectin exhibits crystallinity, as shown by the X-ray patterns of waxy maize starches (Bear and French, 1941). That no physical measurements, only the iodine-staining characteristics, first indicated the absence of amylose in the waxy-maize starches also suggests that amylopectin is the ordered component (Baker and Whelan, 1950).

Cowie and Greenwood (1957b) showed, by means of acid attack on the granule, that the outside of the granule is composed mainly of amylopectin. Acid attack takes place in two stages, the amorphous region being hydrolysed relatively quickly, while the crystalline portions are much more resistant to chemical attack. It is suggested that the amylopectin has an essentially two-dimensional structure, to allow crystallites to be formed.

Comparison of Starch and Cellulose

It is thought appropriate to mention at this point that cellulose and starch, although very different substances, are chemically related. Throughout the development of starch chemistry comparison has repeatedly been made with the corresponding properties of cellulose. This is certainly so in the case of studies of the thermal degradation of starch.

The chemistry of cellulose is described in detail by Ott and Spurlin (1954), and it suffices here merely to indicate a few salient features. Cellulose is the main structural polysaccharide of plants. It is a long-chain, linear polysaccharide composed entirely of D-glucose residues joined by β-1→4-linkages. It is thus more readily compared with the amylose component of starch, the only difference in structure between the two being the configuration of the 1→4-linkages between D-glucose residues. Although it is thought that, in the plant, cellulose might have a very high molecular weight corresponding to a DP of more than 10,000, when isolated it is generally found to have a DP of about 4,000. The molecular size may therefore be comparable to that of amylose.

Like starch, native cellulose exists in a partly crystalline, partly amorphous form, each cellulose molecule passing through several crystalline and several amorphous regions. The same two-stage effect in reaction with, for example, acid is therefore observed.

SECTION 2 : PHYSICAL AND EXTERNAL CHANGES INDUCED IN STARCH ON HEATING

PHYSICAL AND EXTERNAL CHANGES INDUCED IN STARCH ON HEATING

When starch is heated at temperatures above 250°C, pyrolysis takes place and only a char remains.

At lower temperatures, however, the starch is modified into dextrins. These substances, which have a wide variety of properties depending on the length and severity of the dextrinization process as well as the starch source, are important commercially as pastes and adhesives, and in the paper and textile industries as sizes and coatings.

Reaction Characteristics of Dextrinization

Dextrins are prepared by heating starch, either alone or in the presence of an inorganic catalyst, which is generally an acid but may be alkaline. Similar substances may also be prepared by treating a suspension of starch with enzymes or acids. Only the pyrodextrins will be discussed here.

The dextrin industry is a traditional one, based on experience, and the products obtained vary from factory to factory. Little is known of the chemistry of the reactions or of the structure of the products. A whole range of dextrins is manufactured and there is no clear-cut division in properties between them, but rather a gradual change throughout the whole spectrum. It is therefore extremely difficult to classify dextrins, as any classification must necessarily overlap in some aspects. Industrially, dextrins are divided into the following three groups:-

1. White dextrins which are formed when starch is heated at relatively low temperatures (79 - 120°C) for short times (3 - 8 hrs.) in the presence of an acid catalyst, generally hydrochloric. No colour is produced in the dextrin under these conditions.

2. Yellow, or Canary, dextrins which are formed when starch is heated at higher temperatures (150 - 220°C) for longer times (6 - 18 hrs.), again in

the presence of an acid catalyst. A yellow to brownish colour develops in the product.

3. British Gums which are formed when starch is heated at high temperatures (130 - 220°C) for long periods (10 - 20 hrs.) either in the absence of a catalyst, or in the presence of an alkali such as sodium carbonate. A highly-coloured product is obtained.

Although maize, potato and tapioca starches are generally used, dextrins can be made from any starch. The properties of dextrins can be varied depending on the method of manufacture as well as on the starch source. The initial moisture content of the starch, the catalyst used, the temperature and the duration of roasting all influence the resultant product and a dextrin suitable for a specific purpose can thus be made. The manufacturing processes have been described by Wolff (1950) and Gapen and Rathman (1959).

Products are characterized by determinations of paste viscosity, cold water solubility, alkali lability, reducing sugar value and/or colour. The extent of modification increases in the order:- White dextrins < Yellow dextrins < British Gums (Caesar, 1950).

White dextrins appear to be formed by a hydrolytic action, as there is a decrease in viscosity, with time of heating, and an increase in both reducing power and cold water solubility. In general, the dextrin produced is more stable and less inclined to retrograde the further the conversion is taken. This might suggest that unconverted amylose is responsible for the retrogradation.

In the case of the Yellow dextrins, however, although the viscosity decreases with time of dextrinization, the alkali lability passes through a maximum. This is thought to be due to a hydrolytic reaction taking place initially, but complicated transglycosidation and repolymerization reactions

predominating in the later stages of the process.

There is little comparable data in the literature for British Gums, but it is likely that rapid changes in viscosity and alkali lability similar to those for the Yellow dextrins occur. The reactions taking place are therefore also likely to be comparable (Caesar, 1950).

Physical Changes in the Solid

X-ray diffraction studies carried out by Katz (1934) and Katz and Weidinger (1939) gave the first indication of the changes occurring in the dextrinization process. Wheat, potato and tapioca starches, which are examples of A-, B- and C- type X-ray diffraction patterns respectively (see Section 1), were heated at various temperatures between 100° and 220°C for $2\frac{1}{2}$ hours, allowed to regain water at room temperature, and the X-ray diffraction patterns of the products compared with those of the original starches. It was found that two distinct changes in the X-ray patterns occurred. Firstly, although the crystalline patterns of the native starches gradually became less sharp with increasing temperature, at about 180°C the patterns lost their sharpness altogether. Then, at about 220°C an entirely amorphous pattern of a new type appeared. For a particular starch, these changes took place over very small temperature ranges, but the temperatures at which the changes occurred differed for different starches. The temperature at which the first change occurs corresponds to that at which starch is converted into a water-soluble, non-retrograding substance i.e. a dextrin. As heat is evolved at this stage, the reaction must be exothermic.

Katz also found that by dehydrating starches in vacuo over phosphorus pentoxide the X-ray patterns again lost their sharpness. This was regained, however, when the starches were allowed to take up water. It was therefore assumed that water of crystallization was required for a crystalline X-ray

pattern to be obtained, and it was suggested that an anhydridization reaction was responsible for the first irreversible change. Formation of a dextrin would then involve splitting of the starch chains, leaving laevoglucosan end-groups. Although no experimental evidence was put forward until lately this suggestion was generally accepted.

More recently, the physicochemical techniques of differential thermal analysis and thermogravimetric analysis have become generally available for investigating thermal reactions.

In thermogravimetric analysis (TGA) the rate of loss of weight is measured when the sample is heated at a uniform rate, and the weight-loss recorded. Rate constants and energies of activation may then be evaluated from the data obtained (Wendlandt, 1964). Although this technique can obviously yield valuable information on pyrolysis it has not been used to any great extent in the starch field. This is, perhaps, because of experimental difficulties arising from the production of a "syrup" fraction which may condense on the cooler parts of the balance.

More use has been made, in the study of the thermal degradation of starch, of differential thermal analysis (DTA). In this technique, the sample being studied, or a mixture of the sample and a thermally-inert material such as calcinated kaolin or alumina, is heated at a uniform rate. A comparison is made of the temperature of the sample, measured by thermocouples, and that of pure inert material heated in an identical manner. A 'positive' or 'negative' peak is recorded, usually automatically, on the resulting thermogram whenever there is a positive or negative temperature difference between the sample and reference substance. As such a temperature difference is caused by any exothermic reaction taking place in the sample, the occurrence of such reactions, and the temperatures at which they occur, can be determined. (The

thermograms obtained give temperature differences (ΔT) versus the temperature T, and not true differential curves of $\Delta T/t$ versus T, where t is the time).

Although dextrinization, and later pyrolysis, are likely to be complex processes in which bond rupture and volatilization of degradation products may be occurring simultaneously with bond formation, only the net endothermic-exothermic effect can be measured by DTA. Clearly, it would be advantageous to be able to compare data from DTA and TGA experiments, especially if obtained from the same apparatus.

Several factors affect the thermogram obtained by DTA and complicate any comparison of the results obtained by different authors. For example, being a dynamic method, the faster the heating rate, the greater the discrepancy between the real and apparent temperatures of reaction. On the other hand, a high rate of heating emphasises the difference in temperature between the sample and reference substances, and hence larger, sharper peaks are obtained than at slow rates of heating. This is obviously advantageous. In practice, the rate of heating used is generally between 10 and 20°C per minute. The height and width of the peaks obtained, and the apparent reaction temperature, can also be influenced by the design of the sample-holder, the amount of sample, the packing of the substances and the positioning of the thermocouples. Moreover, it is not often possible to find an ideal inert reference material, that is, one which has the same heat capacity and thermal characteristics as the sample being investigated, and which undergoes no physical or chemical change on heating. Experimental procedures for controlling these variables have been put forward (MacKenzie, 1957), and it has been suggested that a controlled atmosphere is particularly important in the thermal analysis of organic materials (MacKenzie and Mitchell, 1962).

Differential thermal analysis has been applied successfully to synthetic

polymers (Kē, 1964) and to cellulose (Schwenker and Zuccarello, 1964). It was found preferable to obtain the thermograms of cellulose in a nitrogen atmosphere rather than in air as the oxidizing atmosphere produced overlapping peaks and poor curves. It has not, however, been used to any great extent in the starch field.

Table 2.1

Differential Thermal Analysis Results

Starch	Endotherms (°C)	Exotherms (°C)	Reference
?	175° (s) 280° (s)	325° (ms)	Costa and Costa (1951)
?	210° (s) 320° (ms)	510° (m)	Perkins and Mitchell (1957)
Rice	110° (m) 260° (vs) 295° (vs)	365° (s) 480° (ms)	Morita (1956 and 1957)
Maize	130° (m) 280 - 310° (s)	330 - 370° (ms) 475° (ms) 525° (m)	Morita (1956 and 1957)
Potato	125° (m) 275 - 305° (s)	410 - 500° (m)	Morita (1956 and 1957)
Pea	155° (m) 260° (ms) 290° (s)	460 - 525° (m)	Morita (1956 and 1957)
?	115° (s)	600° (s)	Varma (1958)

(s) = small; (m) = medium; (vs) = very small; (ms) = medium small.

It may be seen in Table 2.1 that the results which have been obtained by various authors are in poor agreement. Although this must be due, in part, to variation in technique and instrumentation as detailed above, it can also be attributed to non-standardization of operating conditions and differences, both in source and pre-treatment, of the starch samples used.

Many of the starches are not characterized at all, or only poorly; for some, not even the botanical source is given. The endotherm at ca. 120°C varies both in size and in the actual temperature at which it occurs. The variation in size would appear to be a reflection of the different drying procedures used, and it is questionable if this endotherm has any significance other than as a measure of the extent of drying of the sample. If this is so, in no case reported in Table 2.1 was the sample adequately dried. The variations in the thermograms may also be attributed to different heating rates, and to the atmospheres under which these analyses were carried out, some being done in a nitrogen atmosphere and some in air. Oxidation will obviously affect the shape of the thermogram. When nitrogen is used, however, it may be replaced during the run by evolved gases so that the atmosphere is not completely inert throughout. Finally, the "compressed sandwich packing" method has been used to obtain some of these results, i.e. the starch was in contact with "thermally inert" alumina. It has been shown, by measurement of the volatiles produced, that the presence of salts influences the mode of degradation of starch (Bryce and Greenwood, 1966b), and it is probable that any inorganic material would have a similar effect. Morita (1956), in fact, admitted that the use of alumina packing altered the thermograms, but, as irreproduceable results were otherwise obtained, he continued to use this technique.

The limitations which apply to the studies on starch apply also to those on the starch components. A qualified distinction between the components from starches of certain botanical species such as potato was made by Morita (1956). He found, when the samples were analyzed in a nitrogen atmosphere, that the amylose was characterized by one endotherm at 295°C, while the amylopectin had two endotherms, at 230°C and 270°C. Chesters and Thompson (1961) found differences in the exothermic reactions of amylose and amylopectin

in air above 330°C. In addition, these authors suggested that amylose is more thermally stable than amylopectin.

SECTION 3 : DIFFERENTIAL THERMAL ANALYSIS OF MALTODEXTRINS AND OF STARCH AND ITS COMPONENTS

DIFFERENTIAL THERMAL ANALYSIS OF MALTODEXTRINS AND OF STARCH AND ITS COMPONENTS

It was shown in the previous section that the small amount of work which has already been done on the DTA of starch and its components is in poor agreement and open to criticism on a number of points. An attempt has been made here, therefore, to study a number of well-characterized starches and their components under uniform DTA conditions in order to obtain a critical evaluation of its use. In particular, comparisons have been made of the thermograms of:-

1) starch with and without the addition of inorganic material
2) some common starches
3) the starch components, amylose and amylopectin
4) starches containing varying percentages of amylose

In addition, a study has been made of the effect on the thermal stability of the increase in size of the oligomer series G_1 to G_7, where G_1 is glucose, G_2 maltose, G_3 maltotriose etc.

Experimental

DTA Apparatus and Procedure: A Du Pont 900 Differential Thermal Analyzer was used to obtain all the thermograms. A heating element was placed in a silver block equidistant from two chambers, in which were placed tightly-fitting soda-glass tubes, one containing the sample and the other the reference material. A chromel-alumel thermocouple in the centre of each measured the respective temperatures, and the difference in temperature was automatically plotted as a function of sample-temperature on an X-Y recorder. Samples of starch and its components were contained in tubes of 2 mm. external diameter, while the oligomers were packed into tubes of 4 mm. external diameter. The different sizes of tubes were used because the amount of gas evolved from

starch samples in the larger tubes dislodged the sample and destroyed the thermal contact. Alternatively, the amount of a small sugar (which had been freeze-dried and was difficult to pack) which could be put into a 2 mm. tube was not great enough for any temperature-difference to be readily detectable by the instrument.

It was found that a rate of about 10°C per minute, or faster, was required in order to obtain a thermogram with reasonably sharp, well-defined peaks. However, as the discrepancy between actual and recorded temperatures of reaction was very little greater for a rate of 20°C per minute than for 10°C per minute the former, being more convenient, was used throughout. A thermogram recorded at the rate of 20°C per minute could be completed in about 20 minutes. For a given sample, the temperatures obtained for peaks were usually found to be reproduceable to ± 2°C. "Noise" on the thermograms, and the adoption of a higher baseline, were sometimes obtained due to evolution of gases, and loss of sample. However, it was found that these anomalies were generally eliminated, and reproduceability attained, by using a small starch sample, a correspondingly small amount of gas being evolved. Approximately 5 mg. samples were used for the small sugars, and 2 mg. for starch samples.

As the heat of reaction is directly proportional to the amount of reacting substance, the peak area should be proportional to the mass of reacting sample. In practice, this was not found to be so. Although taking care to position the thermocouples in the centre of the sample, and to ensure optimum thermal-contact between thermocouple, sample, and the walls of the sample holder, brought relative peak heights nearer to the theoretical, complete reproduceability was not achieved. This was probably due to disturbance of the system by evolution of gas on decomposition.

The analyses were carried out <u>in vacuo</u>, with continuous pumping to remove

evolved gases, in order to eliminate complications due to oxidation, and to ensure a similar atmosphere for the duration of the run.

Materials Used: The glucose and maltose used were commercial samples. The series of maltodextrins, G_3 - G_7, were kindly supplied by Dr. W. Banks. These sugars, which were prepared by acid hydrolysis of amylose and the paper-chromatographic separation of the hydrolysate, were chromatographically pure.

The potato starch was isolated by the method of Banks, Greenwood and Thomson (1959). Potatoes (var. "Pentland Crown") were thickly peeled, sliced and then minced into 0.1M mercuric chloride solution. After extraction for 2 minutes in an "Automix" blender with the mercuric chloride solution, which inhibits enzyme action, the pulp was filtered through muslin. The filtrate was then centrifuged, the supernatant liquor discarded, and the starch washed by repeated sedimentation in 0.1M sodium chloride solution. The remaining pulp was extracted with saline in the blender three times. After sedimentation the crude starch products were combined. The protein present was denatured by shaking the starch, suspended in saline solution, with toluene overnight. After the starch had settled the toluene layer, containing the protein, was discarded. This process was repeated and the now pure starch then stored in 0.01M sodium chloride solution under toluene at 0°C.

The cereal starches, which were isolated according to Adkins and Greenwood (1966) were kindly supplied by Dr. G.K. Adkins.

The starches were fractionated into amylose and amylopectin by the following method. A starch slurry, sufficient to give a ca. 0.5% solution, was added to water which had been heated to boiling under nitrogen. After boiling for 1 hour the solution was cooled to 60°C and powdered thymol (1 gm. per litre of solution) added. After remaining for 72 hours at room

temperature the amylose-thymol complex was removed in the "Sharples" supercentrifuge and recrystallized from hot n-butanol solution three times. The supernatant liquid, which contained the amylopectin, was extracted with ether to remove excess thymol. Residual ether was removed from the aqueous layer by bubbling nitrogen through it, and the amylopectin precipitated by addition of ethanol.

The characteristics of the starches were:

Potato amylose:

$[\eta]$ in 0.15M KOH = 240, concentration in g/ml.; β-limit = 97% conversion into maltose; iodine affinity = 20.0%;

Potato amylopectin:

$[\eta]$ = 160; β-limit = 56; iodine affinity = 0.2;

Wheat amylose:

$[\eta]$ = 330; β-limit = 72; iodine affinity = 19.8;

Wheat amylopectin:

$[\eta]$ = 150; β-limit = 54; iodine affinity = 0.6.

Results and Discussion

The interesting range of temperatures in the thermaldegradation of a starch is that in which dextrinization takes place, and in which the evolution of gases begins. It was decided, therefore, to study the thermal behaviour at temperatures up to 400°C, with particular attention being paid to the range 250 - 350°C.

The compressed sandwich packing technique has been used by earlier workers (Costa and Costa, 1951; Morita, 1956 and 1957; Perkins and Mitchell, 1957; and Varma, 1958). In this technique, the sample is "sandwiched" between two layers of "inert" material, such as alumina, in order to achieve

better packing of the sample. However, any effect the "inert" material might have on the degradation of the starch has generally been ignored. Since it has been found (Bryce and Greenwood, 1966b) that addition to starch of simple inorganic salts, such as sodium chloride, accelerates the thermal degradation as measured by the study of the evolved gases, and since Morita has admitted that the use of alumina packing altered the thermograms, the effect of alumina on the DTA of starch samples was investigated.

Figure 3.1 shows the thermograms of potato starch alone, and mixed with 10% aluminium oxide. Up to 287°C, the degradation pattern was unaltered by the addition of the alumina, i.e. there was a small endotherm at 275°C, a very small one at 282°C, and an appreciable exotherm at 287°C. Above this temperature, the presence of alumina altered the thermogram appreciably, the large endotherm at 302°C being almost completely suppressed. An exactly similar effect on the thermogram was found when sodium chloride was mixed with the starch. Reproduceable thermograms were thus obtained, under the conditions described above, until well after the evolution of gas had begun.

It may be noted that suppression of the endotherm at 302°C by the inorganic material would explain the acceleration of gas evolution in its presence, an athermal or very slightly endothermic mechanism being possible instead of the normal one, which is pronouncedly endothermic.

Thermograms of Common Starches

Thermograms of potato, maize and wheat starches are shown in Figure 3.2. It can be seen that the general pattern of each thermogram is the same; there is a small endotherm at about 280°C followed by an exotherm in the range 285 - 305°C, and then a large endotherm in the range 302 - 330°C. It was noticeable that the two cereal starches were more stable than potato starch, as shown by the fact that these characteristic temperatures occurred a few

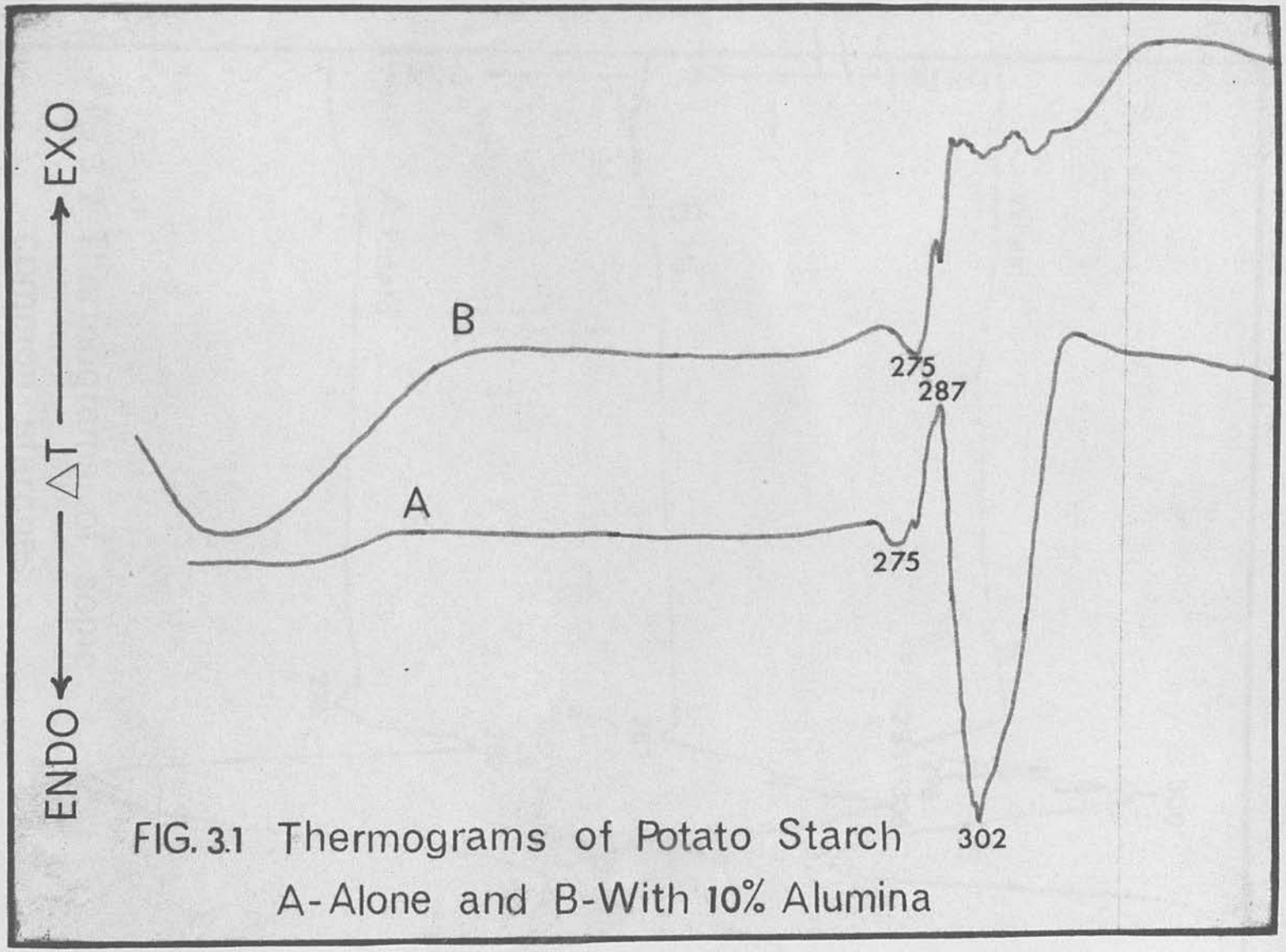


FIG. 3.1 Thermograms of Potato Starch
A-Alone and B-With 10% Alumina

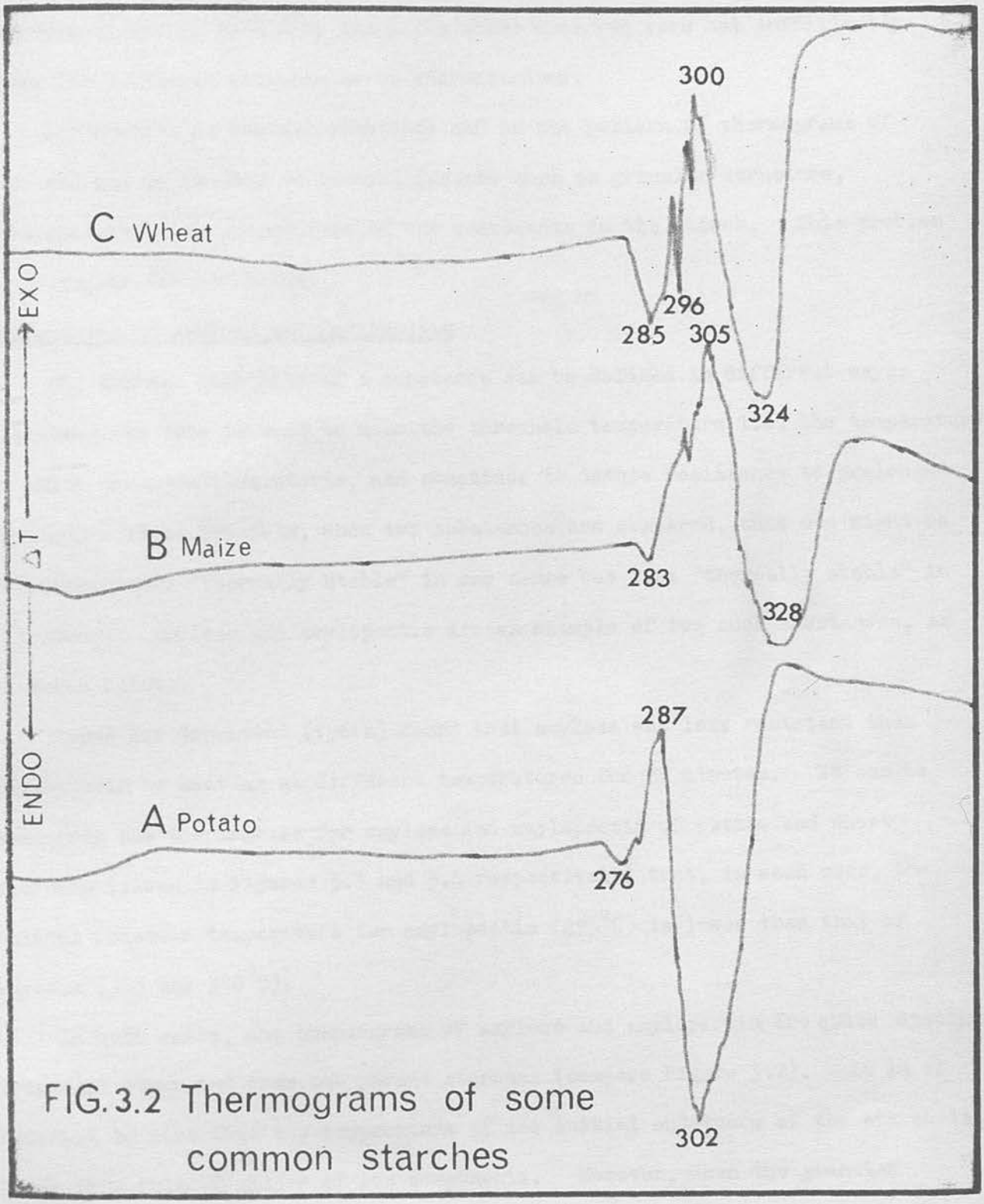


FIG. 3.2 Thermograms of some common starches

degrees higher than the corresponding ones for potato starch. The two cereal starches exhibited very similar behaviour. Although the thermogram temperatures were reproduceable to $\pm$ 2°C, the differences observed were not sufficiently large for different starches to be characterized.

Differences in thermal stability and in the pattern of thermograms of starches may be related to several factors such as granular structure, crystallinity, and proportions of the components in the starch. This problem is discussed further below.

Thermograms of Amylose and Amylopectin

The thermal stability of a substance can be defined in different ways; sometimes the term is used to mean the threshold temperature i.e. the temperature at which decomposition starts, and sometimes to denote resistance to prolonged heating. It is possible, when two substances are compared, that one might be relatively more "thermally stable" in one sense but less "thermally stable" in the other. Amylose and amylopectin are an example of two such substances, as is shown below.

Bryce and Greenwood (1966a) found that amylose was less resistant than amylopectin to heating at different temperatures for 20 minutes. It can be seen from the thermograms for amylose and amylopectin of potato and wheat starches (shown in Figures 3.3 and 3.4 respectively) that, in each case, the initial reaction temperature for amylopectin (295°C) is lower than that of amylose (303 and 306°C).

In both cases, the thermograms of amylose and amylopectin are quite distinct from each other and from the parent starches (compare Figure 3.2). It is of interest to note that the temperature of the initial endotherm of the starch is lower than that of either of its components. However, when the granular structure was destroyed by dissolving the starch in dimethyl sulphoxide and

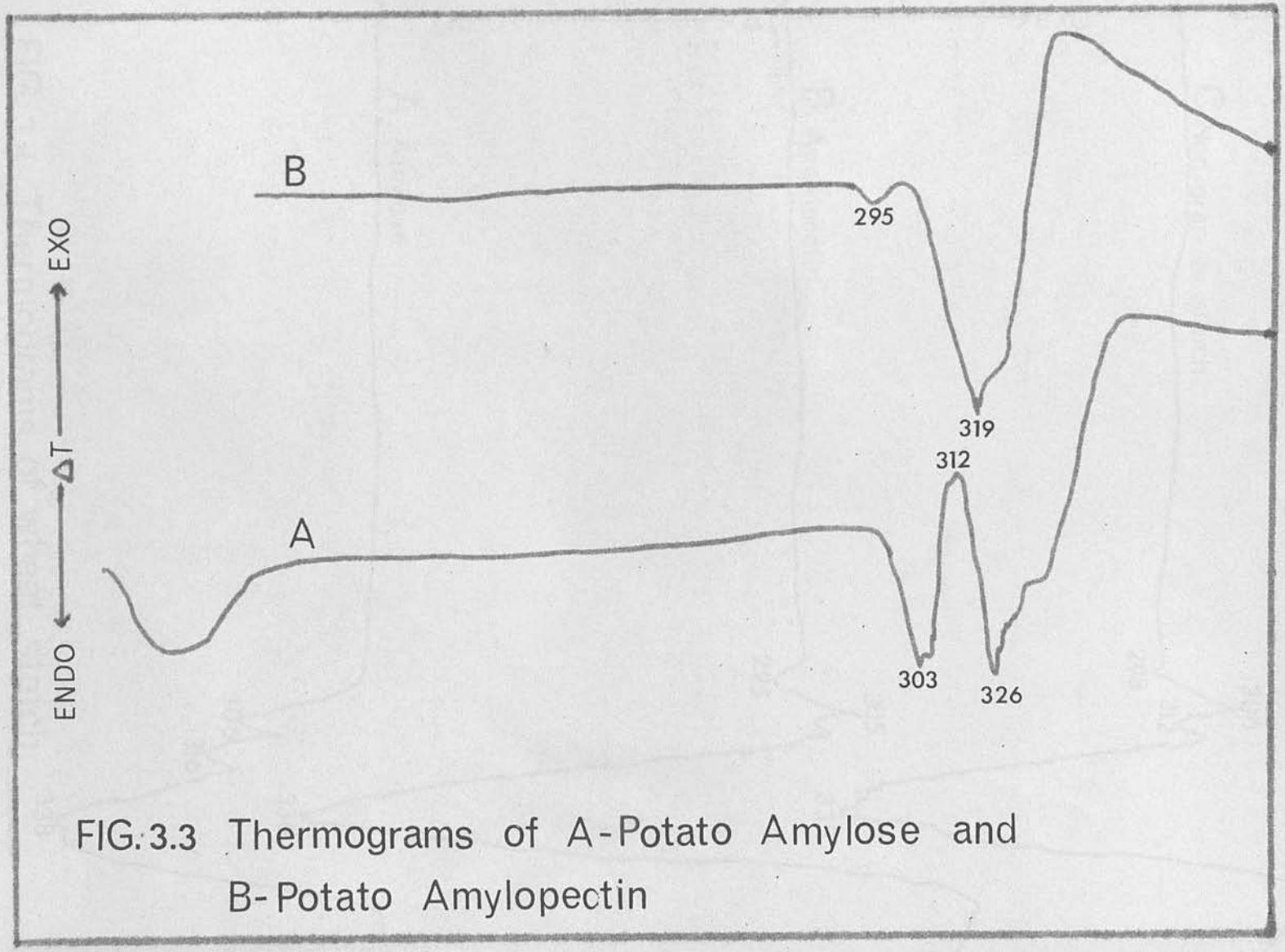


FIG. 3.3 Thermograms of A-Potato Amylose and B-Potato Amylopectin

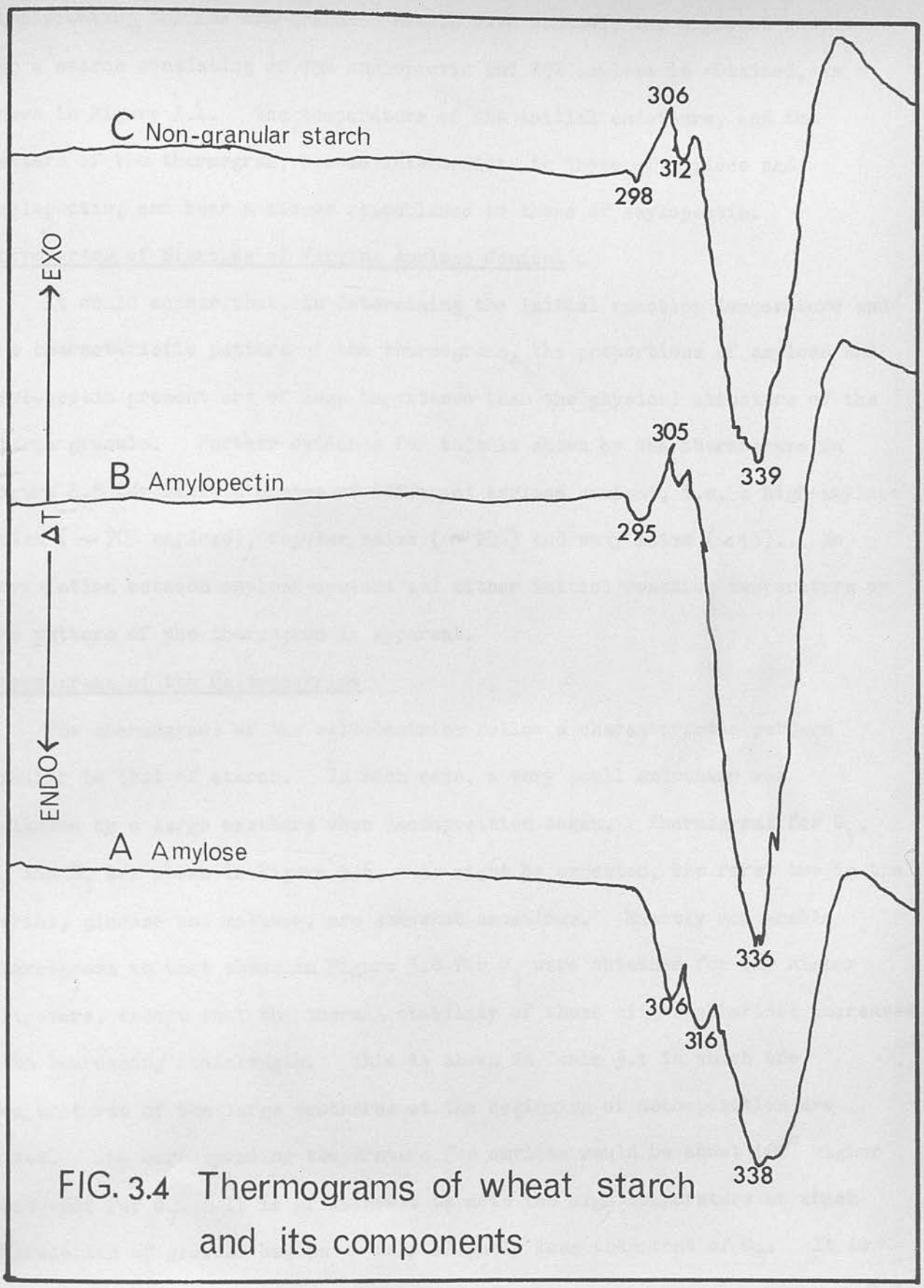


FIG. 3.4 Thermograms of wheat starch and its components

precipitating the now non-granular starch with ethanol, the expected result for a starch consisting of 75% amylopectin and 25% amylose is obtained, as shown in Figure 3.4. The temperature of the initial endotherm, and the pattern of the thermogram, become intermediate to those of amylose and amylopectin, and bear a closer resemblance to those of amylopectin.

Thermograms of Starches of Varying Amylose Content

It would appear that, in determining the initial reaction temperature and the characteristic pattern of the thermograms, the proportions of amylose and amylopectin present are of less importance than the physical structure of the starch granule. Further evidence for this is shown by the thermograms in Figure 3.5 for maize starches of different amylose content, i.e. a high-amylose maize ($\sim$ 70% amylose), regular maize ($\sim$ 28%) and waxy maize ($<$ 1%). No correlation between amylose-content and either initial reaction temperature or the pattern of the thermogram is apparent.

Thermograms of the Maltodextrins

The thermograms of the maltodextrins follow a characteristic pattern similar to that of starch. In each case, a very small endotherm was followed by a large exotherm when decomposition began. Thermograms for G_1, G_2 and G_3 are shown in Figure 3.6. As might be expected, the first two in the series, glucose and maltose, are somewhat anomalous. Exactly comparable thermograms to that shown in Figure 3.6 for G_3 were obtained for the higher oligomers, except that the thermal stability of these oligosaccharides increased with increasing chainlength. This is shown in Table 3.1 in which the temperatures of the large exotherms at the beginning of decomposition are given. The corresponding temperature for amylose would be about 100° higher than that for G_7. It is of interest to note the high temperature at which degradation of glucose begins — only slightly less than that of G_5. It is

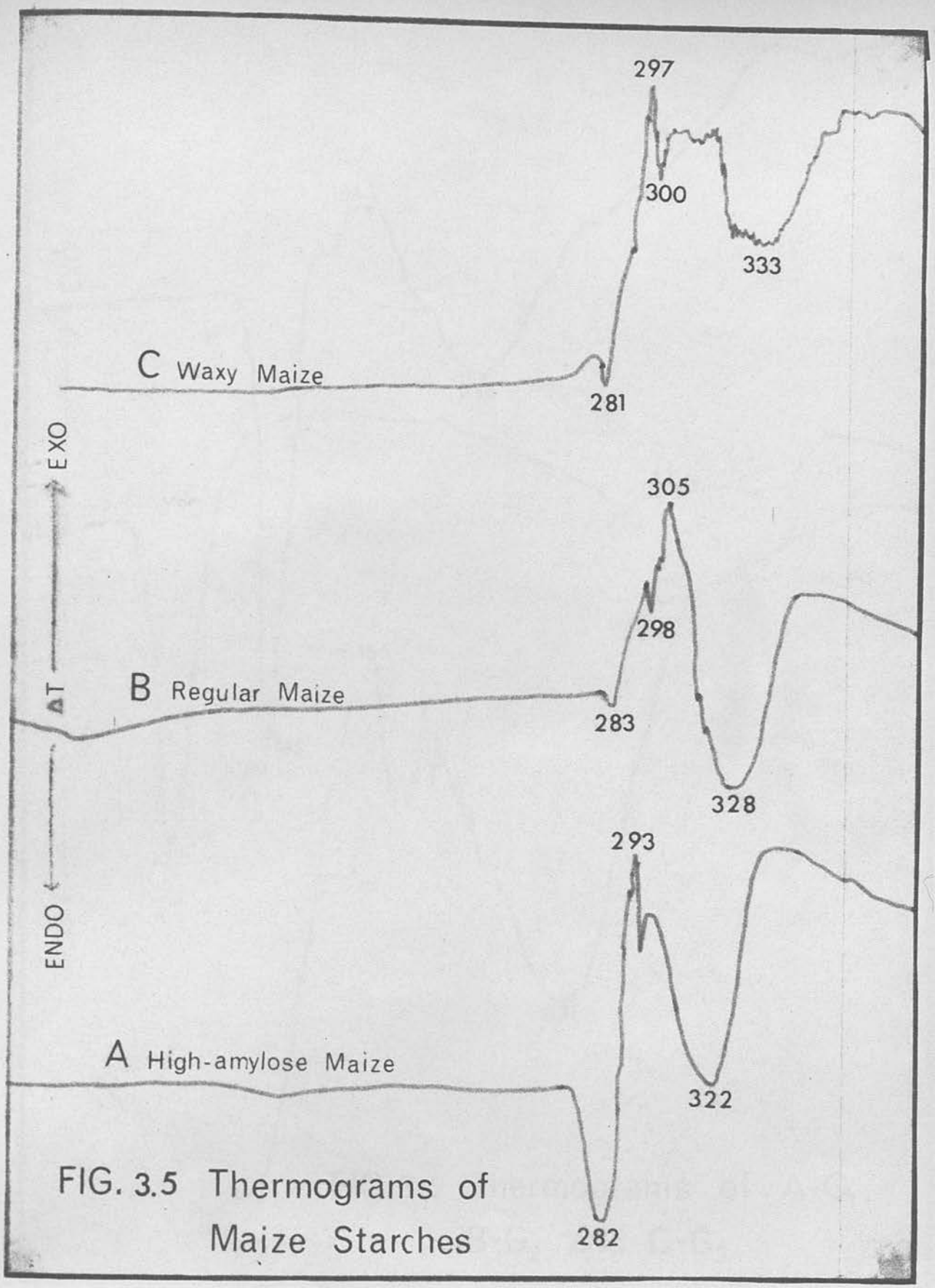


FIG. 3.5 Thermograms of Maize Starches

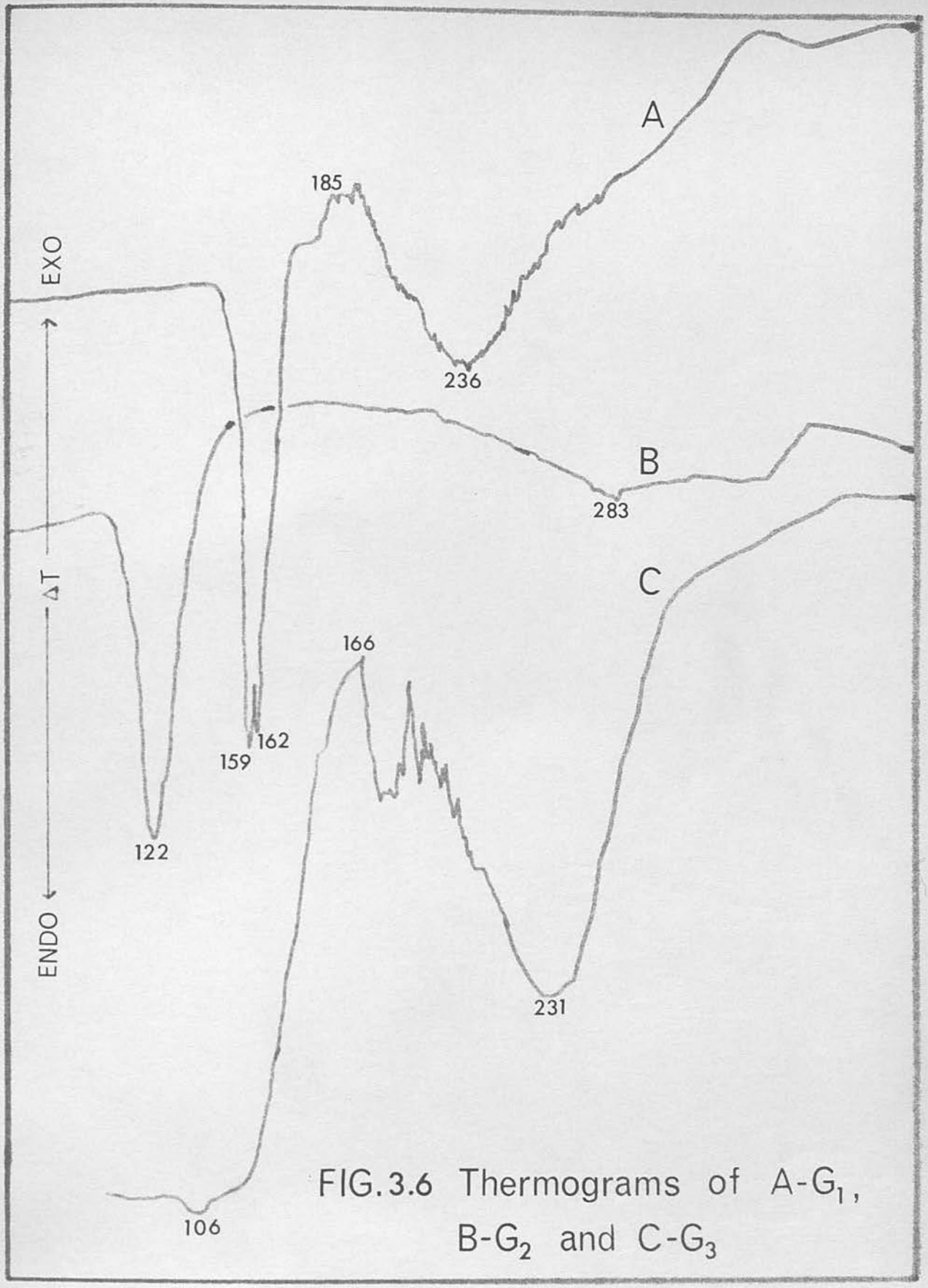


FIG. 3.6 Thermograms of A-G_1, B-G_2 and C-G_3

Table 3.1

Characteristic Exotherms for Maltodextrins

Oligomer	G_1	G_2	G_3	G_4	G_5	G_6	G_7
Exotherm (^{o}C)	185	145	166	180	188	207	220

thus only oligomers of greater than four glucose units in the chain which are clear of the anomalous behaviour associated with the beginning of the series. This will be discussed further in a later section.

Conclusions

It was shown in this section that the presence of alumina profoundly affected the thermogram of starch. DTA should therefore preferably be carried out in the absence of "inert" material. It was also found that the differences in the thermograms of common starches from different botanical sources were not large enough for the different starches to be characterized by DTA. The initial reaction temperature for amylopectin was found to be lower than that for amylose, whilst the physical structure of the starch granule was of more importance than the proportions of amylose and amylopectin in determining the initial reaction temperature and pattern of the thermogram of a starch. The thermograms of the maltodextrins are similar to those of starch, with the thermal stability of the oligomers increasing with chainlength.

SECTION 4 : CHEMICAL CHANGES INDUCED IN STARCH ON HEATING

CHEMICAL CHANGES INDUCED IN STARCH ON HEATING

The Structure of Dextrins

The first studies on the chemical structure of pyrodextrins were made by Brimhall (1944) on a sub-fraction of a commercial British Gum (manufactured from maize starch) which was soluble in 30% aqueous methanol and insoluble in 70% aqueous methanol. This sub-fraction represented 70% of the whole dextrin. Brimhall found, from ferricyanide reducing values, that the average size of the dextrin was about 66 glucose units. Furthermore, methylation and hydrolysis showed only 1 non-reducing end-group in every 12 glucose units of the dextrin, as opposed to 1 in every 24-30 glucose units of the unconverted starch. Brimhall therefore deduced that the dextrin with its average molecular size of ca. 66 units, must have 4-5 branches per molecule. It was also observed that the β-amylolysis limit decreased, with increasing modification of the starch into dextrin, from 55% for the starch to 22% for the final dextrin. This was taken to mean that the external chains of the dextrin had about 5 glucose units each. The resistance of the dextrin to the enzyme from B. macerans, and its failure to produce Schardinger dextrins, was put forward as further evidence that the branches must be made up of less than 6 or 7 glucose units. In view of the many barriers, e.g. an oxidized glucose unit, which are now known to inhibit the action of enzymes such as β-amylase (see Section 1), this interpretation is open to question.

This concept of a small, highly-branched molecule was, however, in accordance with the greater solubility of the dextrin compared with the original starch, and with the iodine titration values, which showed that there was no unbranched component in the dextrin although the unconverted starch had contained 21% of amylose. The equal amounts of periodate consumed by the dextrin and starch showed that the hydroxyls on C_2 and C_3 were not appreciably

changed by dextrinization.

Further studies on the dextrinization of amylose, amylopectin and amylodextrin, as well as granular and retrograded starch, supported the idea of branches being formed. Brimhall therefore suggested a mechanism for dextrinization —— compatible with the results obtained —— which involved two major reactions. Firstly, hydrolysis of the starch to yield fragments of relatively low molecular weight; and, secondly, breaking of glycosidic bonds and recombination with hydroxyls on neighbouring chains. Since the chains are not free to wander about in the dry state, and since the C_6 hydroxyl is most exposed, it was suggested that the branches would most probably form at this position, as shown in Figure 4.1. Although some of the experimental evidence was not conclusive, Brimhall tended to favour the concept of branching rather than that of anhydride formation put forward by Katz (1934; Katz and Weidinger, 1939).

Although Caesar (1950) supported the concept of branch-formation during dextrinization he postulated a different type of branching. It had been found (Caesar, Gruenhut and Cushing, 1947) that a nitrated dextrin had a much lower nitrogen content than the theoretical and, indeed, than that of nitrated starch. In accordance with this evidence Caesar (1950) suggested that ether anhydrides were formed during dextrinization. The linkages were thought to be 6→6, as periodate oxidation results had shown that the hydroxyls at C_2 and C_3 were substantially unchanged. It was suggested that the fact that the alkali lability values of dextrins passed through a maximum, with time of conversion, was support for the theory of formation of laevoglucosan end-groups. The proposed structures are shown in Figure 4.2.

Evidence in agreement with that of Caesar was obtained by Ruggeberg (1952) when he, also, found that nitration of the dextrin became more difficult as

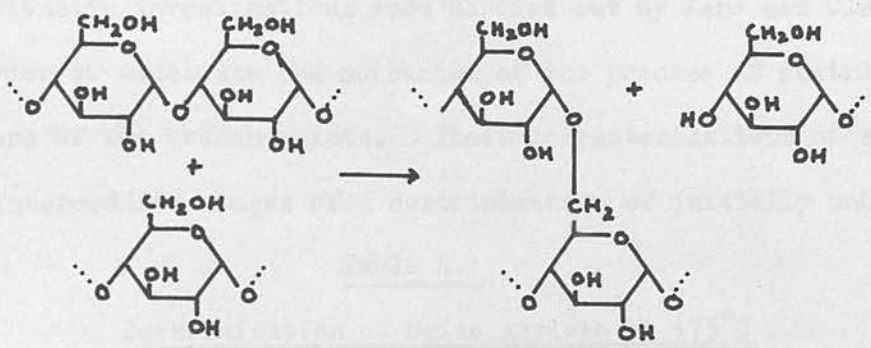


FIG. 4.1 Transglycosidation

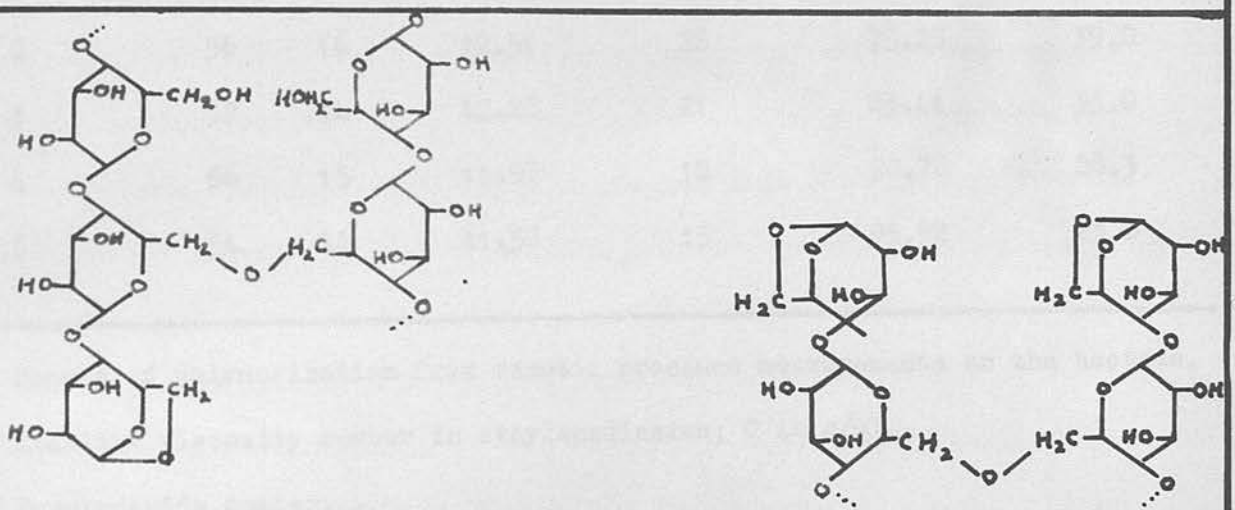


FIG. 4.2 Proposed Ether-linkage Structures

the product became more highly modified. He observed, in addition, that an increase in viscosity occurred during the last stage of roasting, and that the reducing value passed through a maximum during dextrinization.

More extensive investigations were carried out by Kerr and Cleveland (1953) in order to elucidate the mechanism of the process of dextrinization and the nature of the branch-points. Their characterizations of samples, removed at intermediate stages of a dextrinization of initially unbranched

Table 4.1

Dextrinization of Maize Amylose at 175°C

Reaction time (hr)	DP[a]	η [b]	Reducing power[c]	β-Amylolysis limit[d]	Solubility[e]	% Linear material[f]
0	235	65	2.13	95	0.39	99.0
1	58	15	11.63	36	59.28	48.3
2	56	16	12.51	28	75.28	39.0
3	57	14	12.28	21	83.41	33.0
4	56	15	11.98	18	90.78	28.3
5	54	16	11.58	15	95.92	23.0

[a] Degree of polymerization from osmotic pressure measurements on the acetate.

[b] Limiting viscosity number in ethylenediamine; C in g/ml.

[c] Ferricyanide number.

[d] Conversion into maltose.

[e] Solubility in cold, butanol-saturated water.

[f] From iodine-staining measurements.

maize amylose, are shown in Table 4.1. The drop in degree of polymerisation, the decrease in viscosity and the increase in reducing power in the first

hour show that hydrolysis took place initially. As dextrinization progressed, the linear character of the amylose appeared to decrease, as indicated by the increase in solubility and the decrease in both the β-amylolysis limit and the iodine-staining ability. However, after the first hour, the degree of polymerisation remained essentially unchanged. Kerr and Cleveland, believing that the achievement of an equilibrium between hydrolysis and polymerisation would be purely fortuitous, interpreted these results as generally bearing out the Brimhall theory (Brimhall, 1944) i.e. that the major reaction involved is a transglycosidation, a relatively labile 1→4-α-glucosidic linkage being exchanged for a more stable type. Further support for this theory was obtained from their experiments on commercial dextrins. In these, they compared the amount of formic acid produced by periodate oxidation of a dextrin prepared under conditions favourable towards hydrolysis with that produced from a series of British Gums prepared under conditions unfavourable towards hydrolysis. The results clearly indicated that the British Gum dextrinization resulted in a progressive increase in the number of branches.

Kerr and Cleveland (1953) also emphasized that the physical form was important in dextrinization, crystalline and retrograded amyloses being converted into dextrins much faster than amorphous or frozen gel ones. Similarly, they presented evidence that the reported resistance of dextrins to complete nitration (Caesar, 1950; Ruggeberg, 1952) was probably due not to the chemical structure of the dextrin but to its physical state. Although they were unable at first to attain the theoretical tri-acetyl content of commercial dextrins by conventional acetylation methods, it was later achieved by swelling the dextrin prior to the acetylation procedure. They deemed it unlikely, therefore, that the branch-linkages were of the ether-type postulated by Caesar (1950) and Ruggeberg (1952).

. The complexity of the branching structure of the dextrins was demonstrated by Smith and his co-workers. Four commercial maize dextrins were fractionated from aqueous ethanol and the sample which was found to be most resistant to periodate oxidation subjected to methylation and hydrolysis. Column chromatography of the hydrolyzate showed it to contain the methylated sugars listed in Table 4.2 (Geerdes, Lewis and Smith, 1957). After similar treatment, amylopectin would yield only components 1, 2 and 5 in quantity, and amylose only components 1 and 2. Dextrinization must therefore involve considerable transglycosidation and the development of a highly branched structure.

Table 4.2

Results of Column Chromatography of Hydrolyzate of Methylated Maize Starch Dextrin

Component	O-Methyl derivative of glucose	Yield (%)	Mole ratio
1	2,3,4,6-tetra	16.5	35
2	2,3,6-tri	57.3	123
3	2,3,4-tri	2.6	6
4	2,4,6-tri	1.2	3
5	2,3-di	6.3	14
6	2,6-di	10.0	21
7	3,6-di	3.2	7
8	2-	1.5	3
9	3-	0.8	1.7
10	6-	0.5	1

Similar results were obtained by Christensen and Smith (1957) from a study

of the constitution of a wheat starch dextrin. The major fraction obtained from aqueous ethanol was purified by acetylation, and the regenerated sample subjected to periodate oxidation, sodium borohydride reduction and acid hydrolysis. This showed, as did methylation and hydrolysis of the sample, that the average chain length in the dextrin was about 8 glucose units. Moreover, the hydrolyzate of the methylated dextrin contained the same products as those shown in Table 4.2.

The first actual identification of any of the linkages at a branch-point was made by Thompson and Wolfrom (1958). The product, which they obtained on heating a commercial amylose at 185 - 200°C in the absence of acid catalyst, was partially hydrolysed with acid, and the resultant sugars characterized as their crystalline acetates. The isolation of the acetates of maltose, isomaltose, gentiobiose (6-β-D-glucopyranosyl-D-glucose), sophorose (2-β-D-glucopyranosyl-D-glucose), and 1,6-anhydro-β-D-glucopyranose furnished direct evidence that α-D-(1→6), β-D-(1→6), β-D-(1→2) linkages and 1,6-anhydro-β-D-glucopyranose end-groups existed in the dextrin. Identical treatment of the unheated amylose, yielding only the acetates of glucose, maltose and maltotriose (4-α-maltopyranosyl-D-glucose), showed that only α-D-(1→4) linkages were present before dextrinization.

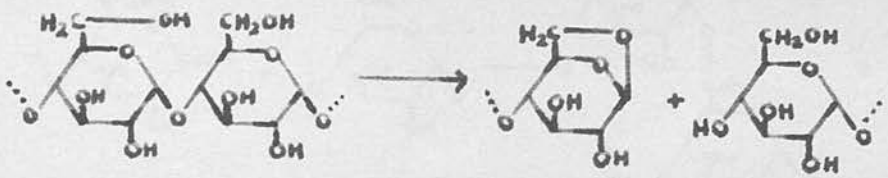
Thompson and Wolfrom (1958) supported the mechanism of transglycosidation put forward by Brimhall (1944) and shown in Figure 4.1. They also postulated two additional mechanisms. The first consisted of attack by the primary hydroxyl at C_6 on the glycosyl bond of the same glucose unit, resulting in chain rupture and the formation of an anhydro-end-group. In the second mechanism, the glycosyl link would be attacked by other hydroxyl groups in the polymer molecule, probably, but not necessarily, the primary hydroxyl of the adjacent glucose unit. This would produce 1→6 linkages, for the most part,

without branching. These reactions are illustrated in Figures 4.3A and B respectively.

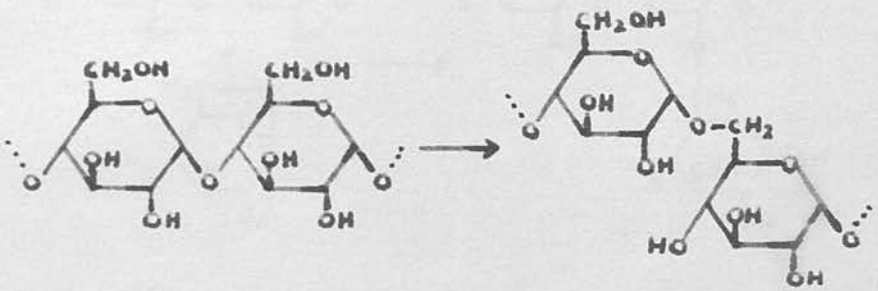
This reaction scheme was extended after further investigations on pyrodextrins by Wolfrom, Thompson and Ward (1961). Measurements were made of the acidity, the copper reducing number, the amount of periodate consumed and the amount of formic acid liberated when samples of commercial amylose were heated at temperatures between 100 and 200°C, both in the presence and absence of acid catalysts.

Maxima were found in the periodate oxidation versus temperature and in the reducing-power versus temperature for the acid-catalysed samples. This is indicative of the occurrence of opposing reactions. Transglycosidation reactions, such as those shown in Figures 4.2 and 4.3A and B, would form more end-groups and result in an increase in both periodate uptake and formic acid liberation. Any scission reaction, such as that shown in Figure 4.3C would also have this effect. The opposing reactions postulated for causing the reduction in periodate uptake are shown in Figure 4.4. In reversion (A), a potential aldehyde group of one polymer molecule reacts with a primary alcohol group of another polymer molecule to form a 1→6 linkage. Recombination (B) involves the interaction of an anhydro-end-group with either C_2, C_3 or C_4 of a glucose unit in an adjoining chain.

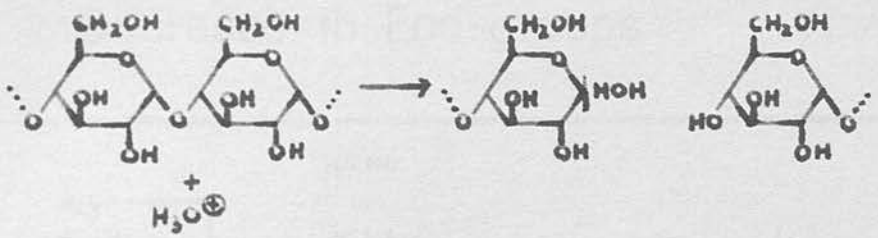
It was proposed that dextrinization under acid conditions took place, in addition to the hydrolysis-reversion mechanism, by the degradation of 1,6-anhydro-end-groups followed by recombination. Moreover, it was suggested that, in the case of dry, unacidified starch, the hydrolysis-reversion mechanism played a minor role, and the linkages were altered by first degrading to 1,6-anhydro-end-groups followed by reaction of this end-group with a hydroxyl group.



A

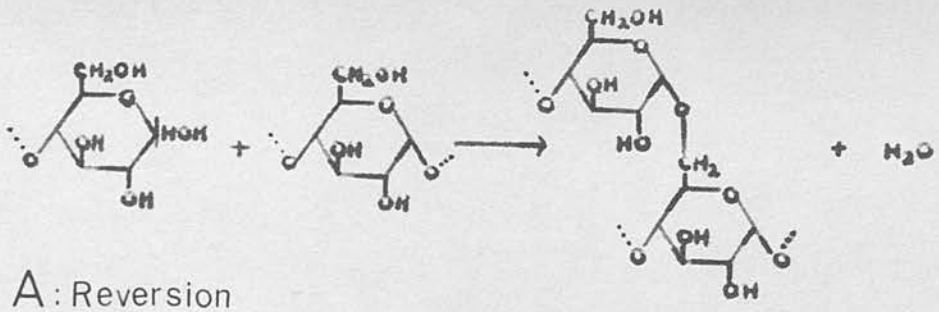


B

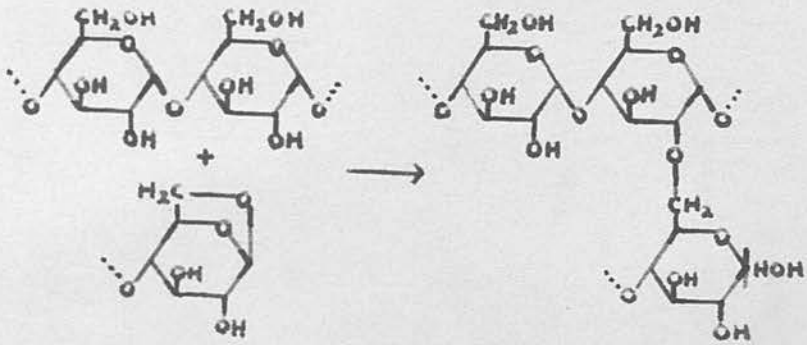


C

FIG. 4.3 Proposed Reactions Causing an Increase in End-groups



A : Reversion



B : Recombination

FIG.4.4 Proposed Reactions Causing a Decrease in End-groups

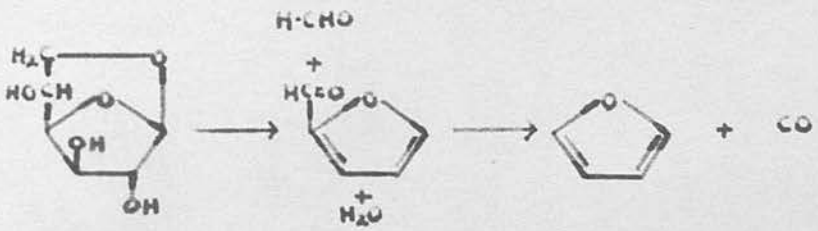


FIG. 4.5 Proposed Reaction for Formation of Furan

Evidence that polymerization can take place from a 1,6-anhydro-end-group was obtained by Wolfrom, Thompson and Ward (1959) in a study of the behaviour of laevoglucosan on heating. It was already known that 1,6-anhydro-β-D-glucose can polymerise when heated under suitable conditions (Pictet, 1918; Carvalho, Prins and Schuerch, 1959). Wolfrom et al., using the procedures already reported for amylose dextrins, isolated, from the partial acid hydrolysate of the laevoglucosan polymer, gentiobiose, isomaltose, maltose, sophorose, cellobiose (4-β-D-glucopyranosyl-D-glucose) and 1,6-anhydro-β-D-glucose. This shows the presence of α- and β-D-(1→6), α- and β-D-(1→4), β-D-(1→2) linkages and 1,6-anhydro-β-D-glucopyranose end-groups. Later work (Wolfrom, Thompson, Ward, Horton and Moore, 1961) characterized di- and trisaccharide portions containing the anhydro-end-group. It is of interest that no 3-D-glucopyranosyl anhydrodisaccharides, nor any 3-O-D-glycosyl linked substances were encountered. It was suggested, from the results obtained in this work, that dextrinization of starch at high temperatures might be a depolymerization destroying an α-D-(1→4) linkage with the formation of a terminal anhydro-group, followed by repolymerization to produce other glucosidic linkages. The molecular weight distribution of the laevoglucosan polymer was calculated by Abe and Prins (1961) from a comparison of the number-, weight-, and Z-average molecular weights. They also suggested, from theoretical considerations, that the α-D-(1→6)-linkage is the one most readily formed.

A highly-branched polymeric product containing both (1→4)- and (1→6)-linkages is obtained on heating D-glucose in the presence of acid catalysts (Durand, Dull and Tipson, 1958; Mora and Wood, 1958; Mora, Wood, Maury and Young, 1958).

Pyrolysis Products of Starch

When starch is heated to temperatures higher than those of dextrinization,

violent decomposition occurs. For ease of analysis, the decomposition products are generally divided into three, easily-distinguishable groups i.e. a) the involatile residue — the "char", b) material of low volatility — the "syrup" fraction, and c) the highly volatile products.

The relative amounts of each formed depend not only on the temperature and time of heating but also on the presence or absence of inorganic materials and on the pressure in the system. Many investigations are carried out *in vacuo* in order to remove the products immediately from the heated reaction zone and so diminish secondary reactions.

Little work has been done on the nature of the char which remains after pyrolysis of starch, but it is likely that it is mainly carbonaceous in character. The percentage weight of residue, with respect to original weight of polysaccharide, after heating for 20 minutes at different temperatures, has been used to estimate the relative thermal stabilities of starch and its components and of cellulose (Bryce and Greenwood, 1966a). The results in Table 4.3 show that cellulose is relatively more stable than starch, and the order of thermal stability appears to be amylose < starch < amylopectin < cellulose.

Table 4.3

Thermal Stability of Starch and Cellulose[a]

Temperature (°C)	219	251	277	300	337
Amylose	94	50	18	11	9
Starch	93	58	25	12	10
Amylopectin	94	60	30	12	8
Cellulose	94	94	72	12	8

[a] Percentage by weight of polysaccharide remaining after heating *in vacuo* at the

given temperature for 20 minutes. Results from Bryce and Greenwood (1966a).

Measurement of the residual weights of starch after 18-hour pyrolyses *in vacuo* at different temperatures showed that a rapid increase in the rate of decomposition occurred between 220 and 250°C (Bryce and Greenwood, 1963b). This temperature is lower than that reported in Section 3 for the initial reaction temperature, obtained from differential thermal analysis. This is presumably due to the great differences in the experimental conditions, DTA being a dynamic method as opposed to the static method employed by Bryce and Greenwood. This change in the rate of decomposition was accompanied by a change in the infra-red spectra of the pyrolytic residues. At 200°C the spectra corresponded to that of the original starch, while from 220°C upwards they corresponded to that of the syrup.

The infra-red absorption spectra of chars obtained from the pyrolysis of cellulose at different temperatures have also been studied (Hofman, Ostrowski, Urbanski and Witanowski, 1960). It was found that the aliphatic structure began to disappear rapidly above 300°C and was gradually replaced by an aromatic condensed system. Indeed, at 525 - 575°C, the infra-red absorption spectra were very like those of anthracite and graphite.

The "Syrup" Fraction

Bryce and Greenwood (1965), using an original type of molecular still, made a quantitative estimation of the syrup produced on the pyrolysis of various saccharides. It was found that the yield of syrup was in the order of glucose > maltose and maltotriose > starch, amylose and amylopectin > cellulose. This was in the reverse order of the thermal stabilities estimated from residual weights. It was assumed that the syrup consisted of 1,6-anhydro-β-D-glucose only.

It is probable, however, that the syrup fraction is a complex mixture of pyrolytic decomposition products. The first identification of any component was made in 1918 when Pictet and Sarasin isolated laevoglucosan from the dry distillation, under reduced pressure, of starch, cellulose, maltose and D-glucose. More recently, the 1,6-anhydroglucofuranose has also been isolated (Bryce and Greenwood, 1963b; Dimler, Davis and Hilbert, 1946; Sawardeker, Sloneker and Dimler, 1965; Gardiner, 1966).

Sawardeker, Sloneker and Dimler (1965) achieved a quantitative analysis of the two anhydroglucoses by gas-chromatographic analysis of the trimethylsilyl ethers. They found that the proportions of the two anhydroglucoses produced from the pyrolysis of waxy-maize starch depended on the moisture content of the starch. Dry starch yielded 19% 1,6-anhydroglucopyranose and 0.9% 1,6-anhydroglucofuranose, whilst starch containing 11.8% moisture yielded 12% and 0% respectively.

The syrup fractions obtained from the pyrolysis at 300°C of potato starch and its components was found to contain furfural (Bryce and Greenwood, 1963b), which was identified by its specific reaction with aniline in glacial acetic acid to form a red complex. The pyrolysis of amylose at 300°C has also been shown to yield 1,4:3,6-dianhydro-D-glucopyranose (Bedford and Gardiner, 1965). The structure of this product was assigned on the basis of proton magnetic resonance spectra.

In a more extensive study, Gardiner (1966) detected, by gas chromatography of the trimethylsilyl ethers, the products already known. In addition, he detected 5-hydroxymethylfurfuraldehyde in the syrup fraction from the pyrolysis of amylose, amylopectin, cellulose, maltose and glucose, and 2-furyl hydroxy-methyl ketone from the cellulose pyrolysis. His quantitative estimation of the yields of the various products are shown in Table 4.4. While the

Table 4.4

Molar yields of pyrolysis products

Compound Pyrolyzed	PRODUCTS				
	A[1)]	B[1)]	C[1)]	D[1)]	E[1)]
Cellulose	38.5	1.5	0.7	1.3	0.6
Amylose	28.8	2.0	1.2	0.4	
Amylopectin	24.7	2.1	1.6	0.4	
Maltose	29.4	4.0	1.0	4.3	
Glucose	19.8	6.9	1.4	2.1	

1) A = 1,6-anhydro-β-D-glucopyranose; B = 1,6-anhydro-β-D-glucofuranose; C = 1,4:3,6-dianhydro-D-glucopyranose; D = 5-hydroxymethylfurfuraldehyde; E = 2-Furyl hydroxymethyl ketone.

quantitative aspect of this work may be open to question, because the conditions of pyrolysis are not well-defined, and the yields depend on both the conditions and scale of the reaction, the qualitative aspect is undoubtedly of value.

Quantitative estimations of the syrup fraction obtained from pyrolysis of cellulose have also been made. Schwenker and Pacsu (1957) found that pyrolysis of cellulose in a limited supply of air at 350 to 375°C yielded *ca.* 70% syrup fraction. Laevoglucosan was confirmed as a major product, constituting 12.5% of this. Madorsky, Hart and Straus (1956) obtained a yield of 52% syrup from the pyrolysis of cotton at 280°C *in vacuo*. The syrup fraction was claimed to consist mainly of laevoglucosan. Similar results have been obtained by

Holmes and Shaw (1961) and by Byrne, Gardiner and Holmes (1966).

The syrup yield from cellulose pyrolysis has been found to be dramatically reduced by the addition of salts such as sodium chloride or sodium carbonate (Madorsky, Hart and Straus, 1956). Addition of glucose has also been claimed to lower the syrup yield on cellulose pyrolysis (Golova, Pakhamov, Anrievskaya and Krylova, 1957), although more syrup is produced from D-glucose than from the other saccharides.

Heynes, Stute and Paulsen (1966) have investigated the pyrolysis of large quantities of D-glucose in a nitrogen atmosphere. Although laevoglucosan was identified among the products, 1,4:3,6-dianhydro-D-glucopyranose was found to be the major product. The total yield of anhydro-sugar was only about 3%. The discrepancy between these and other workers may be due to the different scales used, or to differences in the apparatus and experimental procedure.

Again, high yields of pure laevoglucosan have been claimed when any polymer of D-glucose is pyrolyzed at 350 to 450°C in a stream of gas such as superheated steam (Carlson, 1966).

The above results suggest that the pyrolysis of starch under reduced pressure involves a rapid breakdown of the molecular structure at 220 - 250°C rather than a steady increase in decomposition with increasing temperature. The mechanism is obviously complex and, to date, the knowledge of even the products obtained is limited. Moreover, changing the conditions appreciably changes the products obtained. However, some suggestions as to the mechanism have been put forward. Clearly, production of laevoglucosan must involve scission of a 1→4 glucosidic linkage and anhydridisation. One suggested mechanism, whereby the primary hydroxyl attacks a glucosidic bond to produce an anhydro-end-group has already been shown in Figure 4.3A (Wolfrom, Thompson and Ward, 1961). Gardiner (1966) has postulated that laevoglucosan might be

formed, from both amylose and cellulose, by concerted displacement mechanisms, facilitated by conformational changes in the glucopyranose units.

The reaction mechanisms occurring in the pyrolysis of cellulose are no more understood than those for starch. It has been suggested that the first, and rate-determining, step is the depolymerization of the cellulose to laevoglucosan (Parks, Esteve, Gollis, Guercia and Petrarca, 1955). Although several suggestions have been put forward for the reactions occurring both with and without added salts, none is generally accepted (Broido and Kilzer, 1963; Byrne, Gardiner and Holmes, 1966; Holmes and Shaw, 1961; Madorsky, Hart and Straus, 1956).

The Minor Volatile Products

The first study of the volatile compounds produced when starch is pyrolysed was carried out by Puddington (1948). It was found that, in addition to the major volatile products of carbon dioxide, carbon monoxide and water, small quantities of acids, aldehydes and volatile solids were produced. Similar results were found on pyrolysis of cellobiose, maltose and glucose. To identify a mixture containing small amounts of a large number of compounds was exceedingly difficult by the conventional chemical and physical techniques available at that time, and it is only since the advent of gas chromatography that much progress has been made in the characterization of these compounds.

The first application of this technique to the minor volatile products of starch pyrolysis produced chromatograms with poor resolution because of the presence of a relatively large proportion of water. These preliminary results showed, however, that the volatile products included polar, oxygenated, organic compounds, and aldehydes and furan derivatives were tentatively suggested (Greenwood, Knox and Milne, 1961). Better resolution was obtained in subsequent work by Bryce and Greenwood (1963a). Fifteen compounds were

identified by isothermal gas chromatography after separation from the pyrolyzate of potato starch, which had been heated at 300°C for 15 minutes in a nitrogen atmosphere. These compounds are listed in Table 4.5.

Table 4.5

The volatile products obtained from the pyrolysis of starch and cellulose

Compound	A[1)]	B[1)]	Compound	A[1)]	B[1)]
Carbon dioxide	P	P	Methyl ethyl ketone	P	P
Carbon monoxide	P	P	n-propanol	P	-
Furan	P	-	Water	P	P
Formaldehyde	T	P	Glyoxal	-	P
Acetaldehyde	P	P	Propionic acid	T	-
2-methylfuran	P	-	Acetic acid	T	P
Propionaldehyde	P	P	Formic acid	T	T
Acrolein	P	P	Furfural	-	P
Acetone	P	P	Lactic acid	-	T
n-butyraldehyde	P	T	Diethyl ketone	P	-
Methanol	T	T	Methyl propyl ketone	P	-
2,5-dimethyl furan	P	-	5-hydroxyl methyl furfural	-	P

1) A = products identified by Bryce and Greenwood (1963a) from the pyrolysis of starch and cellulose.

B = products identified by Schwenker and Beck (1963) from the pyrolysis of cellulose.

P = Positive identification T = Tentative identification

- = Not identified

Analyses of pyrolyzates of other polysaccharide materials, obtained under the same pyrolysis conditions, were also carried out. It was found that the chromatograms obtained from different starches, amylose, amylopectin, cellulose, D-glucose, maltose and maltotriose were qualitatively identical. The saccharides which are composed of D-glucose units must therefore all degrade in a similar manner. Other polysaccharides were found to yield different, but characteristic, decomposition products.

Temperature-programmed gas chromatography has been applied to the analysis of the volatile decomposition products of cellulose (Schwenker and Beck, 1963). The results indicated that at least thirty-seven different compounds were evolved. However, only about half of these were identified by retention volume data and functional group analysis. These are listed in Table 4.5. For the most part the compounds identified are the same as those identified by Bryce and Greenwood (1963a).

It is of interest that essentially the same chromatograms were obtained from pyrolysis of the cellulose in air and in nitrogen, only the quantities of products produced differing. This was taken to indicate that the dominant mechanism of decomposition was non-oxidative in character. It was suggested that cellulose depolymerizes at elevated temperatures by scission of 1→4 glycosidic linkages followed by intramolecular rearrangement of the monomer units to form laevoglucosan. According to the hypothesis of Schwenker and Beck (1963), the laevoglucosan would then undergo 1) fragmentation to form volatile, low molecular weight products, and 2) polymerization and aromatization to form char. Glassner and Pierce (1965), who found that there was a close similarity between the volatile products from the pyrolysis of laevoglucosan and of cellulose, supported this mechanism of degradation.

Similar chromatograms have been obtained for cellulose degradation products

both by condensing the volatile products and subsequent gas-chromatographic analysis, and by the "flash pyrolysis" technique where the sample is degraded on a hot wire loop and the decomposition products swept directly onto the chromatographic column (Glassner and Pierce, 1965; Martin and Ramstead, 1961; Schwenker and Beck, 1963). Although the latter technique has not been applied to starch, it has been used successfully as a means of estimating the percentage of 2-hydroxyethyl group in O-(2-hydroxyethyl) starch (Tai, Powers and Protzman, 1964).

A quantitative study of some of the volatiles produced on the pyrolysis of starch and related compounds has been carried out by Bryce and Greenwood (1963b). The amounts of the most important volatile substances produced after 18 hours pyrolysis at 300°C were reported. The rate of production of the same compounds was also determined by quantitative gas chromatography. Although initially, furan and 2-methylfuran were produced in the greatest quantities this was not the case for the summative amounts. It was therefore suggested that furan and furan-derivatives might be primary decomposition products. A possible reaction mechanism put forward for the production of 2-furaldehyde and furan from 1,6-anhydro-α-D-glucofuranose is shown in Figure 4.5.

Some detailed mechanisms have also been postulated for the production of carbonyl compounds (Byrne, Gardiner and Holmes, 1966; Gardiner, 1966). Clearly, the formation of these minor volatile products must be complex, and there is not at present enough data available to elucidate completely the reaction mechanisms.

The complexity of the thermal degradation of saccharides is demonstrated by an investigation of the volatile products from the pyrolysis of 100-gram samples of D-glucose at 300°C in a nitrogen atmosphere (Heynes, Stute and Paulsen, 1966). More than 100 compounds were isolated, of which 56 were identified. Furans were again found to be principal products, with aldehydes,

ketones, diketones and aromatic hydrocarbons also present.

The Major Volatile Products

When starch is pyrolyzed the polymer molecule breaks down into a large number of volatile compounds. Some of these, in particular carbon dioxide, carbon monoxide and water, are produced in much greater amounts than the others, and it is the production of these three compounds which will be discussed in this section.

Various attempts have been made to determine quantitatively the yields of these major volatile compounds and to use the results as a basis for kinetic interpretations. ~~To gain~~ reproduceable results for the yields of the products may be achieved by careful control of the experimental conditions. Kinetic interpretation is, however, rather more difficult. If more than one reaction is involved in the production of one or more of these products, the yield determined will be the sum of the yields from all the reactions. It is possible, not only that these substances might be produced from more than one reaction involving the thermal degradation of starch itself, but also that they might be produced from the breakdown of decomposition products.

Water, at least, is known to be formed in several ways, namely, 1) by removal of residual, bound water, or water of hydration; 2) by dextrinization processes, where reactions such as the formation of anhydro-end-groups liberate water; and 3) by pyrolytic degradation processes, where the D-glucose units are completely broken down into water, carbon dioxide and minor products. Varying the temperature at which the sample is heated might suffice to separate the amounts of water produced from (2) and from (3). It has been found difficult, however, to completely remove water of hydration from a starch sample without simultaneously degrading it. The dextrinization process begins before the starch is completely dehydrated. The retention of water by the starch

granule, and the problem of drying it, are extremely complex (Schierbaum, 1960). Workers in this field have therefore resorted to drying samples under standard conditions so that the results might be readily compared. It is of interest that Murphy (1962) has reported that cellulose cannot be dried completely without simultaneous degradation.

The first quantitative measurements of the yields of carbon dioxide, carbon monoxide and water produced from the pyrolysis of starch were reported by Puddington (1948). Potato starch was heated under vacuum at various temperatures in the range of 180 - 210°C and the amounts of carbon dioxide, carbon monoxide and water liberated were determined by conventional gas-analysis techniques. It was found that a plot of any of the products produced versus time did not give a sigmoid curve. There was therefore no auto-catalysis. The decomposition was reported to be first order, and the ratio of the products was found to be independent of temperature. Graphs of carbon dioxide and carbon monoxide versus water produced were found to pass through the origin, which would indicate, rather surprisingly, that there was no residual bound water remaining after pretreatment of the starch.

The pyrolysis of D-glucose, maltose and cellobiose was also investigated (Puddington, 1948). Cellobiose was found to degrade in a two-step reaction; the first step being dehydration and the second step producing carbon dioxide and carbon monoxide as well as water. Glucose decomposed in a similar manner, after a rapid reaction which was thought to be dimerization. The decomposition of potato starch was similar to the second step of the cellobiose decomposition. The maltose results were anomalous, a constant rate of production of the gaseous products not being achieved.

Two distinct decomposition points were found in the dry distillation of maize, potato and rice starches by Cerniani (1951). Carbon monoxide and carbon

dioxide were formed at the first, at 250°C, and methane and unsaturated hydrocarbons, were produced at the second, about 350 - 400°C.

The production of the major volatile products from the pyrolysis, under vacuum, of potato starch and its components and of cellulose over the wide range of temperature between 156° and 337°C was later studied by Bryce and Greenwood (1966a). The small samples used (ca. 20 mg.) ensured efficient heat transfer throughout the solid, and the use of gas chromatography enabled the small amounts of product to be analyzed quantitatively. The results showed that there was no induction period, autocatalysis or liquid phase present in the decomposition of any of the samples studied. This agrees with the results of Puddington (1948) for potato starch and of Murphy (1962) for cellulose. A sigmoidal curve for the decomposition of cellulose was found by Madorsky, Hart and Straus (1956). This could, however, be attributed to inefficient heat transfer.

Slight decomposition of starch and its components was found to take place at temperatures as low as 156°C (Bryce and Greenwood, 1966a), although it was not until 218.6°C that major decomposition was observed. The corresponding "threshold" temperature for cellulose was much higher, being in the range of 250 to 270°C.

The production of carbon monoxide and carbon dioxide was found to be directly related to the corresponding production of water, and, furthermore, this function became independent of temperature; the point at which temperature-independence was attained differing with the polysaccharide.

Extrapolation of the linear portion of the graph of amount of carbon dioxide or carbon monoxide against the amount of water gave a positive intercept corresponding to 1.0 to 1.5% of water was found for all samples except amylopectin. This amount of water was thought to be residual, bound water,

rather than water from any specific reaction. As all samples had been dried under the same conditions — 15 hours at 65°C under vacuum — before pyrolysis, the retention of water must be least in the case of amylopectin.

Although the ratios of $H_2O:CO_2$ and $H_2O:CO$ both decreased with rising temperature the ratio of $CO:CO_2$ remained constant. The limiting ratios of $CO_2:CO:H_2O$, at high temperatures, were found to be 13:3:1 for starch; 16:4:1 for amylopectin; 10:3:1 for amylose; and 16:5:1 for cellulose. The ratio for starch agreed with that of 3:1 for $CO_2:CO$ quoted by Puddington (1948). It was suggested that, although the decomposition of starch and its components was similar, the thermal stability of cellulose was much higher. This infers, by comparison with the linear amylose, that the β-1→4 linkage is more thermally stable than the α-1→4 linkage.

Energies of activation for the decomposition have been reported. A value of 29 Kcals. $mole^{-1}$ was found for starch (Puddington, 1948; Bryce and Greenwood, 1966a); 30 for amylose; 29 for amylopectin; and 29 for cellulose (Bryce and Greenwood, 1966a). Values for cellulose between 33 and 50 have also been obtained (Madorsky, Hart and Straus, 1956; Murphy, 1962).

The thermal breakdown of cellulose has been the subject of more extensive kinetic investigations. Murphy (1962) found that the decomposition of natural cellulose under vacuum at 100 - 250°C occurred in a two-step process — a slow one referring to degradation of the main structure of the material, and a fast one referring to that of some secondary structure.

A multi-stage process was also suggested by Lipska and Parker (1966). Results from studies of the pyrolysis of cellulose in a nitrogen atmosphere over a temperature range of 250 to 298°C, indicated that an initial, rapid decomposition was followed by a zero-order reaction, and then the decomposition became first order.

Several studies of the thermal decomposition of cellulose have been coupled with investigations of the effect of the presence of inorganic salts, particularly those used as fire retardants (Broido and Martin, 1961; Holmes and Shaw, 1961; Madorsky, Hart and Straus, 1956; Tang and Neill, 1963). It has generally been found that, in the presence of inorganic salts, the initial rate of loss of weight was much greater and the apparent energy of activation was lowered. The salts altered the course of the decomposition in some way, so that a lower percentage of inflammable volatile compounds is produced. The reason for this is not, however, understood.

It had been observed, in early work, that the course of starch pyrolysis also was affected by the presence of salts (Bryce and Greenwood, 1963a). Later, Bryce and Greenwood (1966b) studied the effect of two series of salts on the kinetics of the decomposition of high-amylose maize starch, pyrolyzed in the range of 220 to 240°C. One series of salts had a common anion (the chlorides of copper, calcium, potassium and lithium), the other a common cation (sodium phosphate, borate, chloride and bicarbonate). It was found that each salt lowered the "threshold" temperature of pyrolysis of the starch. Moreover, the apparent activation energy of the degradation process was reduced from 26 kcals. $mole^{-1}$ for the starch alone to between 10 and 13 kcals. $mole^{-1}$ for the mixtures. Each salt also increased the amounts of carbon monoxide and carbon dioxide evolved and changed the shape of the graphs of amounts produced *versus* time. The presence of some salts was also found to change the graphs of carbon dioxide *versus* carbon monoxide produced. It was suggested that the salts must take part in the degradation process rather than acting as catalysts.

SECTION 5 : PYROLYSIS STUDIES ON STARCH AND RELATED COMPOUNDS

PYROLYSIS STUDIES ON STARCH AND RELATED COMPOUNDS

Comparatively few studies have been carried out on the pyrolysis of starch. From the summary given in the previous section, it may be seen that the results obtained were extremely complicated and difficult to interpret. This section describes an attempt to study the pyrolyses of not only starch and its components but also a wide range of "model" and related compounds.

The compounds studied fall into two groups —— oligosaccharides and polysaccharides. The oligosaccharides are the linear α-1→4 linked maltodextrins containing 1 to 7 glucose units. A β-Schardinger dextrin, i.e. a maltodextrin containing a ring of 7 glucose units, has also been studied. The polysaccharides investigated are potato starch, its component amylose and amylopectin, retrograded amylose and bacterialdextran. It was hoped that a comparison of the thermal degradation of amylose and retrograded amylose would show any dependence of the thermal breakdown on physical form. The inclusion of dextran (a glucose polymer linked mainly by α-1→6 bonds, although a few α-1→4 bonds may be present) allowed a comparison to be made of polymers composed of glucose linked by proportions of α-1→4 and α-1→6 bonds varying from approximately 0 to 100%.

EXPERIMENTAL

Pyrolysis and Sampling Apparatus

Description of Apparatus: The pyrolysis apparatus is shown in Figure 5.1. The heating section of the system was designed so that the sample could be pyrolyzed directly after being dried under vacuum, without intermediate exposure to air. This ensured that the sample pyrolyzed was dry and degassed. The pyrolysis vessel, which was detachable from the main system by means of a ball and joint ground glass socket below tap A, consisted of a glass tube joined, by vacuum-tight glass/copper seals, to a copper tube at one end, and to a removable metal flange fitted

with a plunger at the other. Metal parts are shaded in the diagram.

One of the main problems in pyrolysis studies is heat transfer to, and throughout, the sample (Grassie, 1956), the latter being especially important in the case of poor thermal conductors such as carbohydrates. This was overcome by the following means: the copper tube was preheated to the desired temperature by moving the furnace into the position shown in Figure 5.1. before the sample in the bucket was introduced into the pyrolysis position by the plunger; the bucket was made of thin platinum foil and was fashioned into the shape of the tube so that maximum contact was obtained; and the bucket was of such a size that the sample (about 25 mg) could be distributed into a very thin layer over its base.

To prevent catalysis of the pyrolysis products the metal surfaces inside the pyrolysis vessel were gold-plated, and the pyrolysis bucket was made of platinum. Continuous pumping throughout a pyrolysis run by a mercury diffusion pump, backed by an oil pump, removed the products from contact with the residual char and minimized secondary reactions between the products themselves. This enabled pyrolyses to be carried out under a vacuum of 10^{-5} mm mercury. The vacuum was measured by a "vacustat".

The temperature of pyrolysis was controlled to $\pm$ 0.1 C^{o} by a resistance thermometer controller, type "Sunvic" RT2. The copper pyrolysis tube and the temperature gauge of the controller were surrounded by brass shavings contained in aluminium foil to minimize thermal gradients between furnace heater, pyrolysis vessel and resistance controller. The temperature was measured by a chromel-alumel thermocouple, placed against the outside of the copper tube.

Four sets of products were collected:-

1) The char was recovered from the pyrolysis bucket at the end of the run.

2) The syrup fraction was collected by condensation on the cool (room-temperature)

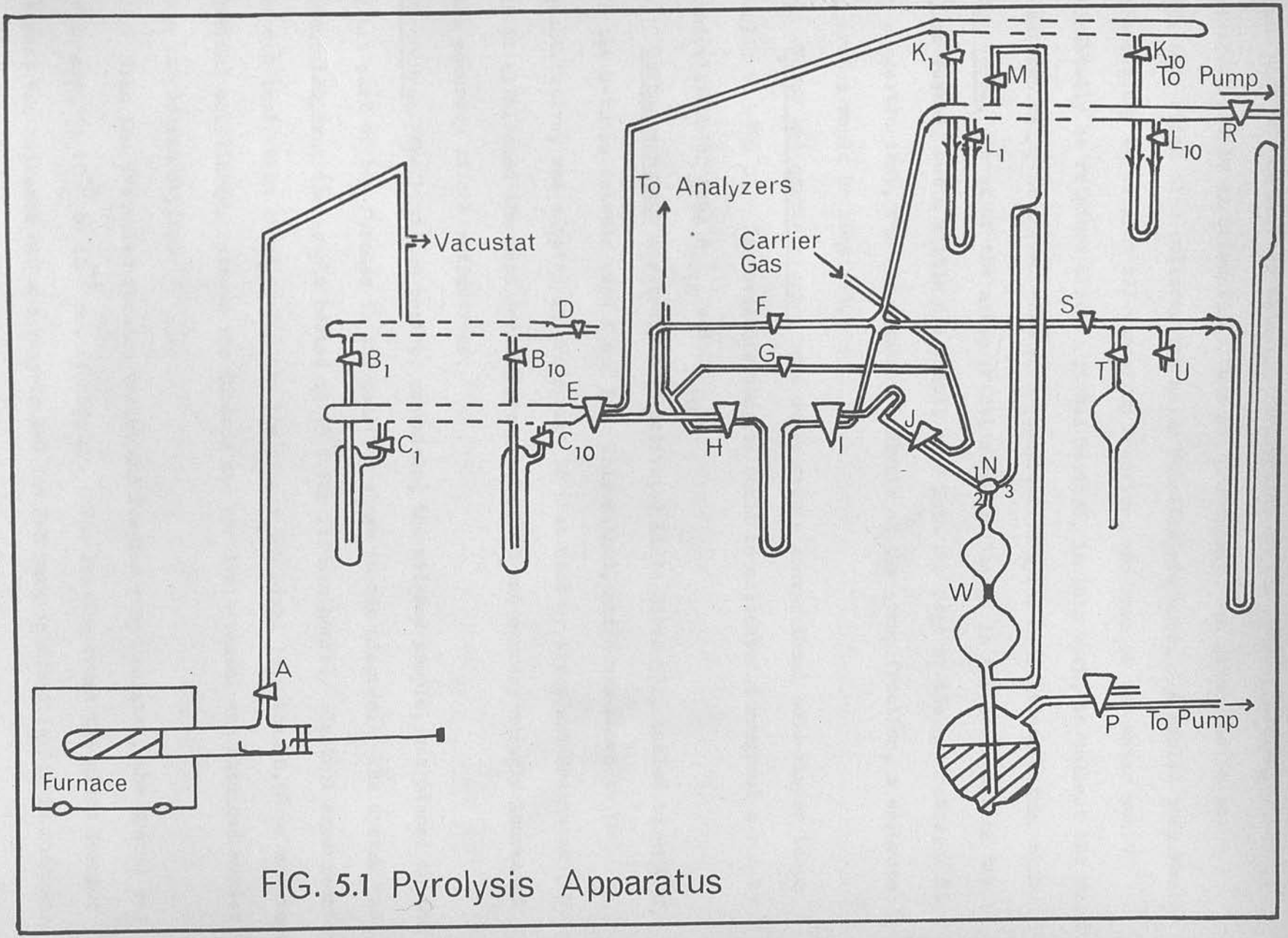


FIG. 5.1 Pyrolysis Apparatus

glass part of the furnace vessel. Collection of the syrup fraction, which is rather difficult experimentally, has not previously been attempted on an apparatus which also collects the major volatile products. A cooled trap would be necessary to collect all the syrup fraction, and some of the water would undoubtedly be retained also. It was decided, in this work, to collect the water quantitatively, at the expense of a quantitative syrup collection, rather than vice versa. Most of the syrup fraction was collected in the cool part of the glass vessel, but a little did distil over into the rest of the apparatus. It is suggested that, for quantitative analysis of the syrup fraction, a separate apparatus would be required.

3) Water and carbon dioxide were collected in conventional cold-finger traps cooled to -192°C. Ten separate samples could be collected throughout a run by manipulation of taps B_{1-10} and C_{1-10}.

4) Carbon monoxide was trapped on activated Linde Sieve 13X, cooled to -192°C, in the U-tubes between taps K and L. This method, which was shown to be quantitative, was adopted in preference to that used by Bryce and Greenwood (1966a), as it eliminated the need for calibration factors and correspondingly increased the accuracy of the estimations.

Procedure: The Platinum bucket, containing the weighed sample, was placed in the glass part of the furnace in the position shown in the diagram. The system was evacuated, and the sample heated to 65°C for fifteen hours. Control experiments showed that under these conditions the sample contained less than 0.1% of moisture. Thermal equilibrium between the furnace and pyrolysis vessel was attained whilst the sample was drying.

With the evacuated furnace vessel and Toepler pump isolated, the system was evacuated to 10^{-5} to 10^{-6} mm. of mercury. The heating round the glass furnace vessel was switched off and vessels B-C and K-L were immersed in liquid nitrogen.

With taps B2 - B10, K2 - K10, S, F and I closed, tap E turned to the top manifold, and taps A, B1, C1 - C10, K1, L1 - L10, and R open, pyrolysis was started by pushing the platinum bucket into the hot metal part of the furnace vessel. At the appropriate time, tap B1 was closed and B2 opened, followed — an arbitrary ten seconds later — by the closing of K1 and the opening of K2. This procedure was repeated for taps B3 to B10 and K3 to K10, so that appropriate amounts of sample were trapped in each vessel.

When the last sample had been collected, taps B10, C1 - C10, K10, L1 - L10 were closed and the boat removed from each oven. When the pyrolysis vessel had cooled, air was allowed into it by opening tap D. The boat was then removed and the weight of pyrolytic residue determined directly.

The syrup fraction was dissolved in methanol, the solvent removed by evaporation at 50°C, and the weight of syrup determined.

Vessels BC1 - 10 were allowed to reach room temperature, and each carbon dioxide and water sample was then transferred in turn into the U-tube HI (at -192°C) by pumping for fifteen minutes via taps E, H and I, with tap F closed. The sample was then volatilized in the U-tube by heating with a glycerol bath at 120°C, and injected into the chromatographic system by taps H and I.

Transfer of the carbon monoxide to the injection system was achieved by means of the Toepler pump. The U-tubes KL1 - 10 were heated in a water bath to about 60°C. The system was evacuated through taps I, H, F and R, taps E, S and M remaining closed. Taps R and F were then closed and taps M and L1 opened. The carbon monoxide was allowed to equilibrate into the Toepler pump. With tap N closed, the mercury in the pump was driven up to the valve W by atmospheric pressure applied through tap P. The gas which had equilibrated into the lower bulb was now trapped above the valve W. Using the alternative position of the three-way tap P, the mercury was then drawn back down, thus allowing more gas into

the lower bulb. The Toepler pumping was repeated twenty times so that effectively all of the carbon monoxide was transferred to the bulb between valve W and tap N. Tap H was then closed, tap N opened between leads 1 and 2 and the carbon monoxide driven by the mercury into the volume between taps H and J. The carbon monoxide was then injected into the chromatographic system. This procedure was repeated for each carbon monoxide sample.

Analysis of Major Volatile Products

The carbon dioxide and water were transferred to the U-tube HI and analyzed by gas-liquid chromatography. Similarly, the carbon monoxide was transferred to the U-tube and analyzed by gas-solid chromatography. Details of the chromatographic systems are summarized in Table 5.1 and described in more detail below.

Table 5.1

Details of the Chromatographic Systems

For analysis of	Carbon monoxide	Carbon dioxide and water
Column material	Pyrex glass tubing	Pyrex glass tubing
Column size	0.4 x 90 cms	0.4 x 240 cms
Column packing	Linde Sieve 13X	Carbowax 20M on Haloport F
Column temperature	18°C	106°C
Carrier gas	Hydrogen	
Carrier gas flow-rate	50 ml/min	
Detector	"Gow-Mac" Katharometer type NRL	
Bridge current	250 mA	
Recorder	"Sunvic" high-speed potentiometric, type 10S	
Chart speed	60 ins/hr.	

The hydrogen carrier gas, whose flow rate was regulated by a needle valve, was passed in turn through a system of glass baffles, two drying tubes containing

silica gel and Linde Sieve respectively, and the reference arm of the detector. It was then diverted through the by-pass shown in Figure 5.1, or allowed to pick up the sample from the U-tube HI, before passing through the column appropriate for the sample and the second detector arm. The flow rate was measured by passing the carrier gas through a soap-bubble flow-meter (Knox, 1962) attached at the outlet of the system. The flow-meter was disconnected during analyses. In order to facilitate the transfer of water within the system the tubing between the U-tube and chromatographic columns, and between the columns and katharometer, was maintained at about 80°C by means of asbestos-lagged, electrical heating tape. This part of the chromatographic system consisted of capillary tubing of as short a length as possible in order to minimize the amount of dead-space in the system and hence improve the resolution of the chromatograms. Throughout the apparatus the unheated taps and joints were greased with Apiezon L and the heated one with Silicone grease.

The carbon dioxide and water were separated on a column of 10% Carbowax 20M on Haloport F. (This was prepared by dissolving the carbowax in chloroform, adding the Haloport F, mesh-size 30-60, and evaporating the chloroform from the suspension with constant shaking.) The column was conditioned at the operating temperature, 106°C, for 24 hours before use. The carbon monoxide was analyzed on a column of Linde Sieve 13X, mesh size 40-60. Periodically this was reactivated by heating it in an evacuated flask, until evolution of gas had ceased. The Linde Sieve used to trap the carbon monoxide in the U-tubes KL was reactivated in a similar manner.

The well-lagged "Gow-Mac" thermal conductivity detector, or katharometer, type NRL, on which the samples were detected, achieved maximum sensitivity by use of hydrogen as the carrier gas. The recorder was modified so that full-scale deflection corresponded to a 1 mV. signal from the katharometer. In order to

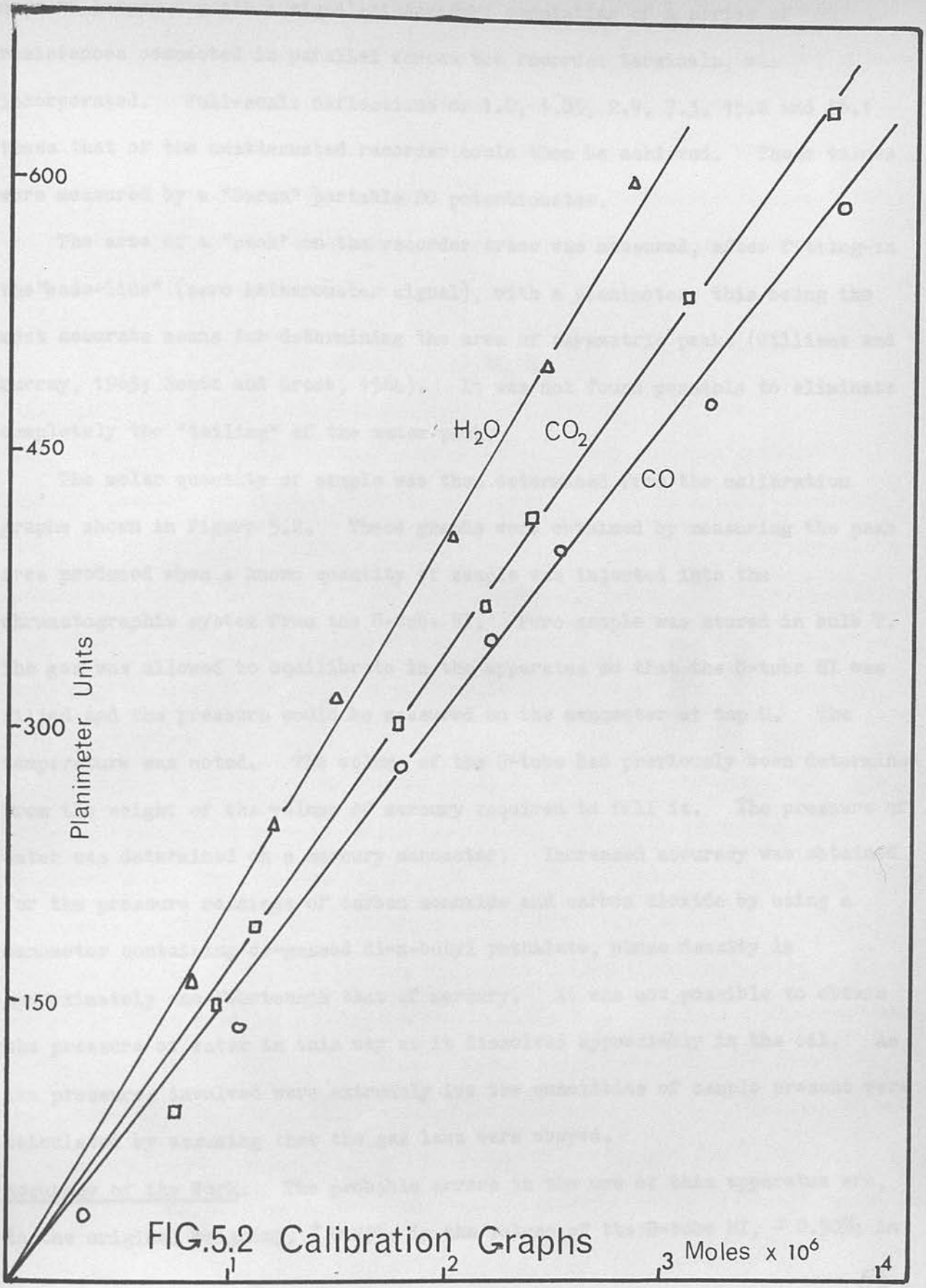


FIG.5.2 Calibration Graphs

measure larger signals a signal-attenuator, consisting of a series of resistances connected in parallel across the recorder terminals, was incorporated. Full-scale deflections of 1.0, 1.85, 2.9, 7.3, 15.2 and 36.1 times that of the unattenuated recorder could then be achieved. These values were measured by a "Doran" portable DC potentiometer.

The area of a "peak" on the recorder trace was measured, after fitting-in the "base-line" (zero katharometer signal), with a planimeter; this being the most accurate means for determining the area of asymmetric peaks (Williams and Murray, 1963; Scott and Grant, 1964). It was not found possible to eliminate completely the "tailing" of the water peak.

The molar quantity of sample was then determined from the calibration graphs shown in Figure 5.2. These graphs were obtained by measuring the peak area produced when a known quantity of sample was injected into the chromatographic system from the U-tube HI. Pure sample was stored in bulb T. The gas was allowed to equilibrate in the apparatus so that the U-tube HI was filled and the pressure could be measured on the manometer at tap U. The temperature was noted. The volume of the U-tube had previously been determined from the weight of the volume of mercury required to fill it. The pressure of water was determined on a mercury manometer. Increased accuracy was obtained for the pressure readings of carbon monoxide and carbon dioxide by using a manometer containing de-gassed di-n-butyl phthalate, whose density is approximately one-fourteenth that of mercury. It was not possible to obtain the pressure of water in this way as it dissolved appreciably in the oil. As the pressures involved were extremely low the quantities of sample present were calculated by assuming that the gas laws were obeyed.

Accuracy of the Work: The probable errors in the use of this apparatus are, in the original weighing, $\pm$ 0.25%; in the volume of the U-tube HI, $\pm$ 0.50%; in

planimetering, ± 1.00%; and in the fluctuation of the flow-rate and bridge-current, ± 2.00%. Estimations of the quantities of carbon monoxide and carbon dioxide are therefore thought to be reliable to ± 4%. The estimations of the quantities of water are, however, slightly less precise because of the difficulty in determining the base-line of the peak, due to the "tailing" effect, and to the less accurate measurement of pressure (with a mercury, not oil, manometer) during calibration.

Analysis of "Syrup" Fraction

Preparation and Analysis of Trimethylsilyl Derivatives: The trimethylsilyl (TMS) derivatives of the "syrups" were prepared by the standard method of Sweeley, Bentley, Makita and Wells (1963), namely:— To 10 mg. carbohydrate dissolved in 1 ml. of anhydrous pyridine (which had been stored over potassium hydroxide pellets) 0.2 ml. hexamethyldisilazane and 0.1 ml. trimethylchlorosilane were added. The mixture, which was in a stoppered vial, was shaken vigorously for about 30 seconds and was then allowed to stand for at least 5 minutes at room temperature.

In order to diminish the solvent peaks in subsequent chromatography, the pyridine was removed by evaporation and the TMS derivative dissolved in petroleum ether (fraction b. pt. 60 - 80°C). This solution was also evaporated to dryness *in vacuo* and the TMS derivative finally dissolved in chloroform.

The details of the Pye 'series 104' model 24 gas chromatograph on which the TMS derivatives were analyzed are shown in Table 5.2. In this design the carrier gas was divided between two identical columns and flame ionisation detectors, one acting as a reference and the other as a detector column. The columns were used alternately. About 2 - 5 μl of sample were required for analysis.

Xylitol was used as an internal standard because of its desirable retention

Table 5.2

Details of the Chromatographic System for Analysis of TMS Derivatives

Column material	Pyrex glass tubing
Column size	0.6 x 160 cms.
Column packing	n-poly-glycol adipate
Column temperature	125°C
Carrier gas	Oxygen-free nitrogen
Carrier gas flow rate	45 ml/min
Detectors	Flame ionisation
Recorder	Speedomax W

time (Sawardeker, Sloneker and Dimler, 1965). The substances were identified by the ratio of their retention times to that of xylitol. The values found for such ratios are:- α-D-glucose, 2.7; 1,6-anhydro-β-D-glucopyranose, 2.9; 1,6-anhydro-β-D-glucofuranose, 3.5; β-D-glucose, 6.1. Although the two peaks merged when both α-D-glucose and 1,6-anhydro-β-D-glucopyranose were present in a large amount, the presence of glucose could still be detected on the chromatogram by the β-D-glucose peak. More specific identification was achieved by the enzymic method described below. On these chromatograms, peak areas were calculated from peak height times peak width at mid-height.

Enzymic Assay of Glucose: The method is described by Banks and Greenwood (1967a). β-glucose is oxidized, by glucose oxidase, to gluconic acid with the liberation of hydrogen peroxide. Peroxidase uses the peroxide to oxidize O-dianisidine to the corresponding imine which is estimated by measuring the optical density of the protonated form at 540 mμ. The determination is carried out in the presence of 0.3 M tris buffer at pH 7.0 containing 40% (v/v) glycerol in order

to suppress the action of maltose-splitting impurities in the enzyme.

This method was also used to estimate the anhydroglucose content of a syrup. A portion of the sample was refluxed for 1 hour with dilute sulphuric acid, in order to hydrolyze the anhydroglucoses, and then the acid removed by shaking with the weak anion resin, Amberlite IR 45, in the hydroxyl form. The glucose content was then determined by enzymic assay. Subtraction of the amount of glucose originally present, determined on a separate portion, then gave the amount of anhydroglucose in the sample. Although this method is not specific for anhydroglucose, but merely for substances which, on hydrolysis, yield glucose, it may be taken as specific for anhydroglucose in circumstances such as these where the presence of other glucose-yielding substances is extremely unlikely.

Analysis of "Char" Fractions

Chars were analyzed for carbon and hydrogen by Drs. Weiler and Strauss of Oxford.

Materials Used

The starch studied in the following sections was isolated from potato, as were the amylose and amylopectin. Their preparation and properties, and those of the maltodextrins, have already been described in Section 3. Retrograded amylose was obtained by injecting a highly-concentrated solution of amylose in dimethylsulphoxide into excess water. Dextran, molecular weight about 10,000, was kindly supplied by Mr. P. Daniels of the Arthur D. Little Research Institute. The β-Schardinger dextrin was provided by Professor W.J. Whelan of the University of Miami and the reference samples of 1,6-anhydro-β-D-glucopyranose and 1,6-anhydro-β-D-glucofuranose by Mr. D. Gardiner of the Shirley Institute. The anhydrofuranose was stored as the triacetyl derivative. Before use it was

FIG. 5.3 Chromatogram of the TMS ether of a small sugar syrup

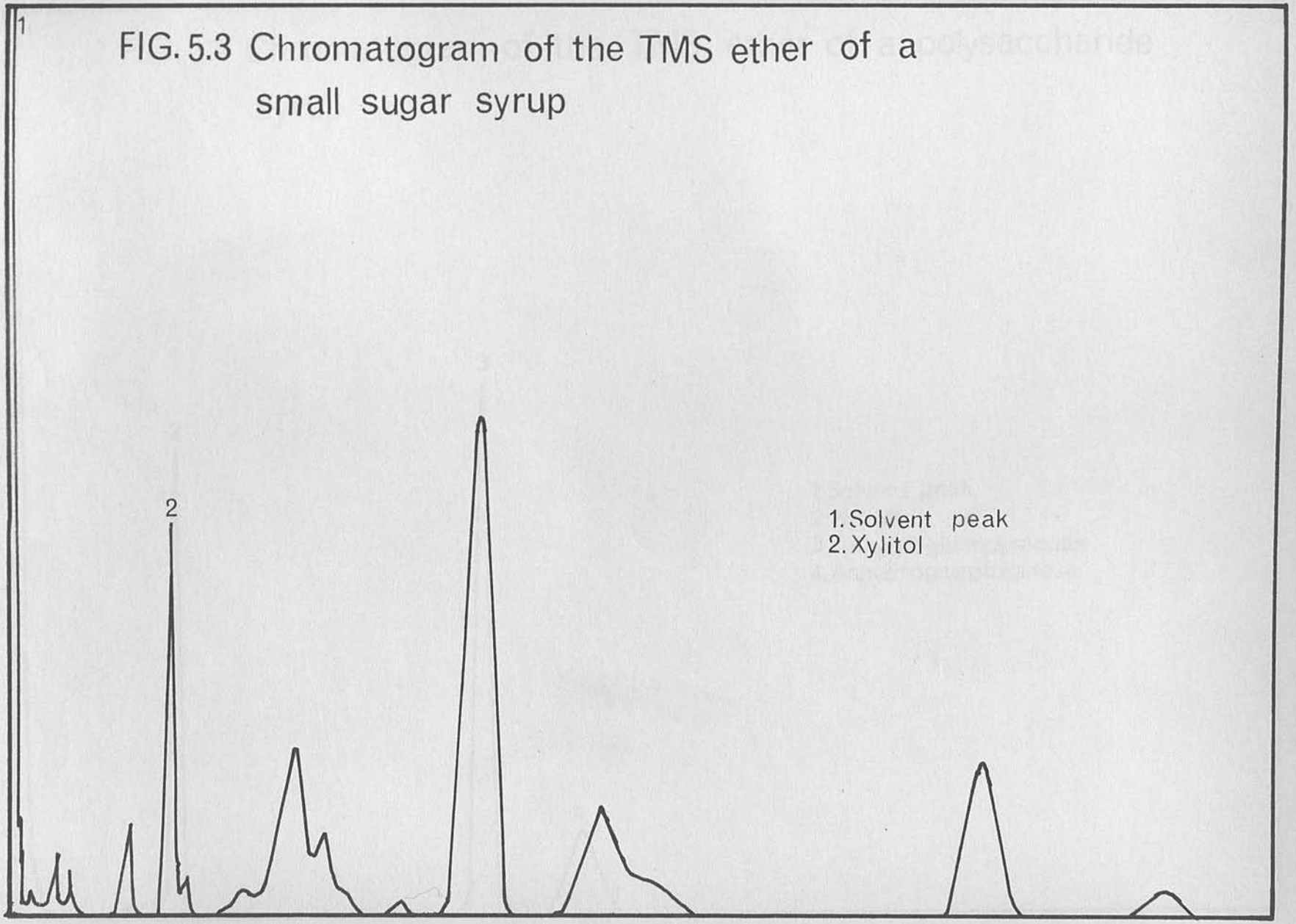
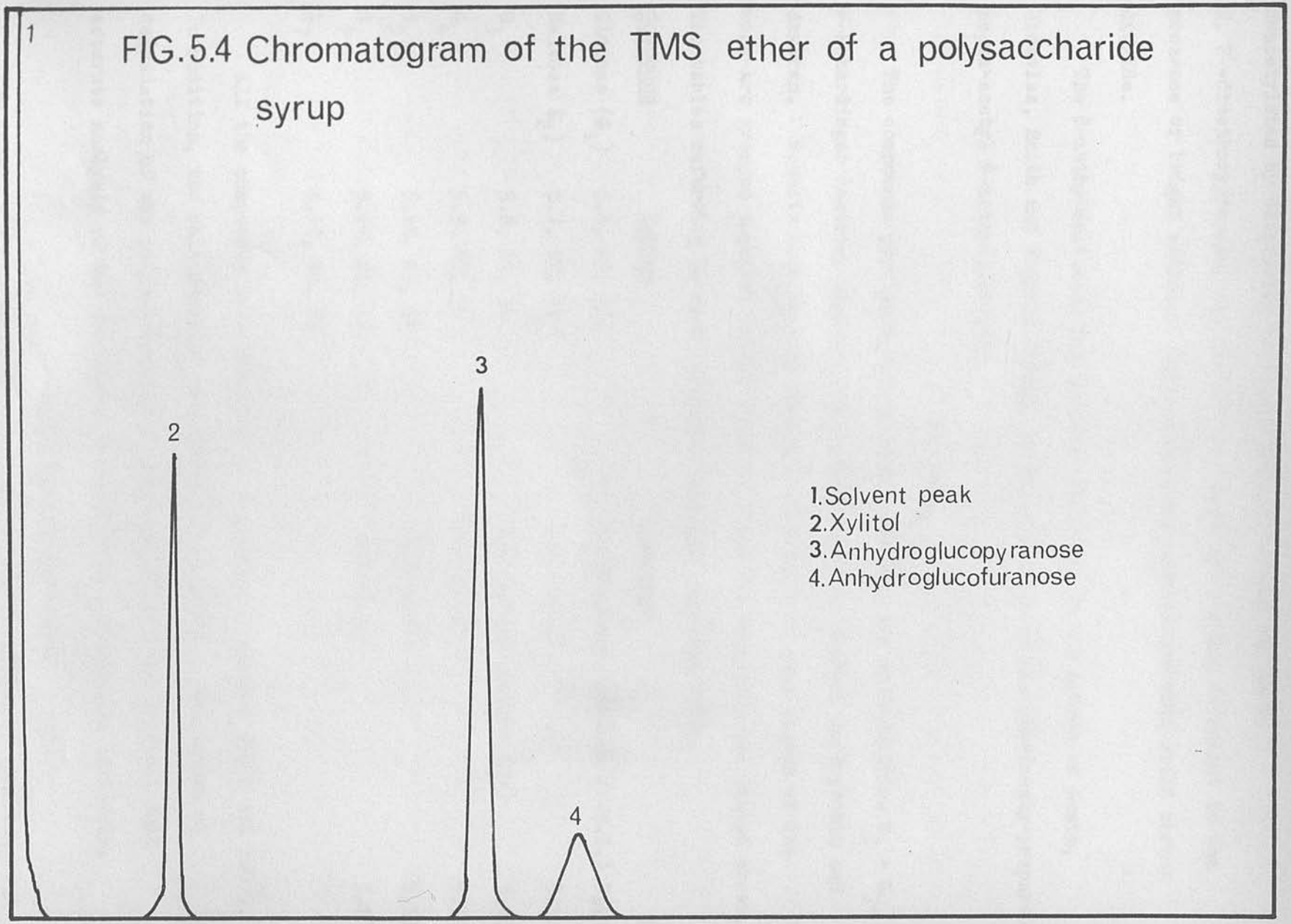


FIG. 5.4 Chromatogram of the TMS ether of a polysaccharide syrup



deacetylated by dissolving it in methanol containing 10% (v/v) 2, 2'-dimethoxypropane, shaking for two hours and leaving overnight in the presence of bright sodium. The solution was neutralized with solid carbon dioxide.

The β-methylmaltoside was prepared according to the method of Newth, Nicholas, Smith and Wiggins (1949), by deacetylation of the previously-prepared hepta-acetyl β-methylmaltoside.

RESULTS

The compounds pyrolyzed were glucose, maltose, the maltodextrins G_3 - G_7, β-Schardinger dextrin, amylose, retrograded amylose, starch, amylopectin and dextran. Results have been so arranged that those in each aspect of the work are grouped together in the order in which the compounds are listed above. The tables referring to each particular compound are list below.

Compound	Tables	Compound	Tables
Glucose (G_1)	5.6, 19, 32.	β-Schardinger Dextrin (β-S.D.)	5.13, 26, 3
Maltose (G_2)	5.7, 20, 33	Amylose (A)	5.14, 27, 4
G_3	5.8, 21, 34	Retrograded Amylose (RA)	5.15, 28, 4
G_4	5.9, 22, 35	Starch (S)	5.16, 29, 4
G_5	5.10, 23, 36	Amylopectin (Ap)	5.17, 30, 4
G_6	5.11, 24, 37	Dextran (D)	5.18, 31, 4
G_7	5.12, 25, 38		

All the compounds were pyrolyzed at temperatures between 250°C and 300°C. In addition, the maltodextrins were pyrolyzed at 225°C. The amount of degradation of the polysaccharides at this temperature was so small that accurate analysis of the amounts of decomposition products was difficult.

Total Products Estimated

The total products estimated after 122 minute pyrolyses of each compound

at varying temperatures are shown in Table 5.3. The products are each expressed as a percentage (weight/weight) of the original sample; it was assumed that the percentage unaccounted for experimentally consisted of minor volatile products, although it is possible that a little of the 'syrup' fraction may be included in these values.

'Char', 'Syrup' and Minor Volatile Products

The weights of pyrolytic residues remaining after pyrolyses for 122 minutes are shown in Table 5.3. The results of carbon and hydrogen analyses, carried out where sufficient residue was available, are shown in Table 5.4, both as percentages of the total and as the molar ratios, carbon : hydrogen : oxygen.

The weights of the 'syrup' fractions recovered after 122 minute pyrolyses are also shown in Table 5.3. Analysis of these syrups by the glucose oxidase method showed that the syrups obtained from the pyrolysis of glucose contained 50-60% glucose. The glucose content of the syrups decreased rapidly with increasing chainlength of the substrate, only 3-10% of the maltose syrups and about 1% of the G_3 syrups consisting of glucose. No glucose was found in the syrups from saccharides with a chainlength of 4 or more.

Gas chromatographic analysis of the TMS ethers of syrups was also carried out. Two distinct types of chromatogram were obtained. The chromatograms from the oligosaccharides of chainlength 5 or less exhibited a complicated pattern of a dozen peaks, as shown in Figure 5.3. These complex chromatograms were thought to arise from the formation of epimeric and mixed dimers of minor pyrolysis compounds and it was not possible to estimate these on the one chromatographic system. In contrast, only two peaks appeared on chromatograms from the syrups of G_6, G_7, β-Schardinger dextrin and the polysaccharides. Those peaks corresponded to 1,6-anhydro-β-D-glucopyranose and 1,6-anhydro-β-D-glucofuranose. A chromatogram, typical of those yielded by the polysaccharide

syrups, is shown in Figure 5.4. For those syrups which consisted entirely of anhydroglucose the ratios of anhydropyranose: anhydrofuranose were calculated from the peak areas, assuming that the peak area per mole was the same for the two compounds. The ratios, which are shown in Table 5.5, were independent of the temperature of pyrolysis. The chromatogram of the TMS derivatives of syrup obtained from β-methylmaltoside showed two predominant peaks, corresponding to 1,6-anhydro-β-D-glucopyranose and β-methylglucoside.

Major Volatile Products

Tables 5.6 to 5.18 contain the amounts of carbon monoxide produced with time for pyrolyses of each saccharide at varying temperatures. The values shown were obtained by summing the fractions in U-tubes KL1-10. The results obtained for the simultaneous production of carbon dioxide and water are shown in Tables 5.19-5.31 and 5.32-5.44 respectively. These yields are all expressed as moles x 10^6 of product per gramme of initial sample. Figures 5.7, 5.8 and 5.9 illustrate the general shape of the curves which were obtained for the production of the major volatiles with time for all the samples over the range of temperature studied.

Figure 5.5 shows graphs of both the carbon dioxide and of the carbon monoxide produced, versus the simultaneous water production for the pyrolysis of G_7 at 300°. It may be seen that, in both cases, a straight-line relation is attained at the later stages of decomposition. Extrapolation of the straight-line portions of the graphs produces a common intercept on the water-production axis. Again, the shape of these graphs was typical. The ratios of water:carbon dioxide:carbon monoxide corresponding to these linear portions are given in Table 5.45.

The rates of production of carbon monoxide at each temperature, given in Table 5.46, were calculated from the maximum slope of the graphs of

(continued on p 87)

Table 5.3

Percentage Yields of Products

Sample	Temperature (°C)	Residue	Syrup	Minor Volatiles	Water	Carbon Dioxide	Carbon Monoxide
Glucose	222.3	29	34	29	8	0.3	0.1
	248.7	15	42	31	10	1.5	0.2
	277.0	9	45	36	8	1.8	0.3
	300.3	8	17	67	6	1.8	0.4
Maltose	222.3	52	7	34	6	0.3	0.1
	248.3	36	17	34	10	2.6	0.5
	277.7	25	28	31	13	3.3	0.7
	299.4	21	21	42	12	3.7	0.8
G_3	222.3	53	12	21	11	2.7	0.6
	248.2	44	4	37	11	3.4	0.6
	277.0	28	21	40	7	3.3	1.1
	301.0	30	5	49	10	5.1	1.0
G_4	222.3	53	4	31	9	2.9	0.7
	248.3	49	2	37	8	3.4	1.0
	272.0	32	32	20	10	4.9	1.2
	299.1	30	5	51	8	4.4	1.3
G_5	222.3	63	9	15	10	2.7	0.5
	249.3	62	1	25	9	2.6	0.8
	277.0	40	9	33	11	6.3	1.1
	299.6	40	9	31	11	7.1	1.5
G_6	222.3	70	4	19	6	1.4	0.3
	248.5	70	1	18	9	1.7	0.5
	277.7	33	21	34	7	3.7	1.1
	299.6	39	17	27	11	5.2	1.0
G_7	222.3	72	10	10	6	1.4	0.4
	248.5	61	9	19	8	2.5	0.8
	277.0	30	18	35	9	6.0	1.8
	300.9	33	23	26	10	6.2	1.9
β-Schard-inger Dextrin	249.9	96	0	4	0.4	0.1	0
	277.7	19	56	19	3	2.4	0.8
	300.3	17	48	26	5	3.3	1.2
Amylose	222.3	88	6	6	0.1	0.1	0
	248.0	90	5	3	1	0.2	0.1
	275.7	40	29	23	6	1.5	0.8
	300.3	20	43	25	8	3.7	0.6
Retrograded Amylose	248.0	88	1	11	0.4	0.2	0.1
	277.5	33	52	12	2	1.0	0.2
	300.5	12	53	27	5	2.5	0.8

Table 5.3 (cont.)

Starch	248.6	60	20	16	3	0.9	0.1
	277.7	27	44	23	4	1.8	0.5
	301.5	21	49	17	8	3.7	1.0
Amylopectin	248.8	92	4	3	0.7	0.3	0.1
	277.6	36	36	20	5	2.3	0.7
	299.0	19	52	18	6	3.3	1.0
Dextran	249.3	89	3	7	1	0.5	0.1
	277.5	42	28	20	6	4.0	0.9
	299.0	26	38	21	9	4.9	1.1

Table 5.4

C-H-O Analyses of Residues

Sample	Temperature (°C)	% Carbon	% Hydrogen	% Oxygen	Molar Ratio Carbon :	Hydrogen :	Oxygen
Glucose	277.0	58.2	4.5	37.3	2.1	1.9	1
G_3	222.3	54.0	5.1	40.9	1.8	2.0	1
	248.2	51.5	4.9	43.6	1.6	1.8	1
	301.0	57.2	4.4	38.3	2.0	1.9	1
G_4	222.3	46.0	4.9	49.1	1.3	1.6	1
	248.3	47.7	4.9	47.4	1.3	1.6	1
	272.0	49.6	4.2	46.2	1.4	1.5	1
G_5	222.3	49.5	5.4	45.1	1.5	1.9	1
	249.3	50.6	5.6	43.8	1.6	2.1	1
	299.6	60.1	4.9	35.0	2.3	2.3	1
G_6	248.5	48.8	5.6	45.6	1.4	1.9	1
	299.6	61.2	4.4	34.4	2.4	2.0	1
G_7	248.5	47.5	5.4	47.1	1.4	1.8	1
	300.9	59.1	5.0	35.9	2.2	2.3	1
β-Schardinger Dextrin	249.9	40.1	6.9	53.0	1.0	2.1	1
Amylose	222.3	41.8	6.7	51.5	1.1	2.1	1
	248.0	43.2	6.5	50.3	1.2	2.1	1
	275.7	48.6	6.3	45.1	1.4	2.2	1
	300.3	63.3	4.9	31.8	2.7	2.4	1
Retrograded Amylose	248.0	40.1	7.3	52.6	1.0	2.2	1
	300.5	45.7	6.2	48.1	1.3	2.1	1

Table 5.4 (cont.)

Starch	248.6	46.9	6.3	46.8	1.3	2.2	1
Amylopectin	248.8	39.9	6.9	53.2	1.0	2.1	1
	299.0	55.8	5.3	38.9	1.9	2.2	1
Dextran	249.3	40.4	6.9	52.7	1.0	2.1	1
	277.5	56.4	5.9	37.7	2.0	2.5	1

Table 5.5

Ratios of anhydropyranose : anhydrofuranose in Syrup Fractions

Sample pyrolyzed	G_6	G_7	β-S.D.	A	RA	S	Ap	D
Pyranose : Furanose	12	11	11	14	12	9	7	7

Table 5.6

Production of carbon monoxide from glucose

T°C / Sample	222.3	248.7	277.0	300.3
1	0	0	7	4
2	2	15	33	19
3	4	27	59	34
4	12	36	70	69
5	20	45	81	82
6	25	58	86	92
7	30	70	104	108
8	34	76	111	115
9	37	83	122	126
10	40	87	125	129
Sample x Timings (minutes)	4x1, 1x2, 1x6, 4x20	4x1, 1x2, 1x6, 2x20, 1x30, 1x40		3x0.5, 1x1.5, 1x3 1x6, 2x20, 1x30, 1x40

Table 5.7

Production of carbon monoxide from maltose

Sample \ T°C	222.3	248.3	277.7	299.4
1	0	11	20	10
2	0	33	50	39
3	0	53	69	65
4	1	69	106	125
5	3	86	134	161
6	7	115	163	194
7	15	153	170	228
8	18	166	184	245
9	20	178	197	260
10	21	188	216	273

Sample Timings as in Table 5.6.

Table 5.8

Production of carbon monoxide from G_3

Sample \ T°C	222.3	248.2	277.0	301.0
1	3	7	71	15
2	30	34	179	53
3	53	57	226	120
4	71	80	242	212
5	86	112	253	244
6	116	156	287	274
7	165	188	335	309
8	184	201	360	331
9	197	210	384	349
10	206	218	404	369
Sample Timings (minutes)	5x2, 1x6, 2x20, 2x30	As in Table 5.6		

Table 5.9

Production of carbon monoxide from G_4

Sample T°C	222.3	248.3	272.0	299.1
1	6	15	39	25
2	39	55	132	115
3	65	109	160	154
4	99	144	215	294
5	118	180	247	336
6	161	241	286	366
7	197	282	325	413
8	219	312	341	440
9	231	336	361	459
10	242	354	379	478
Sample Timings (minutes)	3x2, 2x3, 1x10, 1x20, 2x30, 1x40	as in Table 5.6		

Table 5.10

Production of carbon monoxide from G_5

Sample T°C	222.3	249.3	277.0	299.6
1	16	0	11	17
2	32	4	122	83
3	48	18	132	153
4	63	39	147	234
5	83	67	175	302
6	125	117	256	359
7	164	202	316	430
8	186	237	341	464
9	209	257	370	494
10	225	272	392	520
Sample Timings (minutes)	1x3.5, 1x1.5, 2x2, 1x3, 1x10, 1x20, 2x30, 1x40	As in Table 5.6		

Table 5.11

Production of carbon monoxide from G_6

Sample T°C	222.3	248.5	277.7	299.6
1	0	1	17	0
2	5	3	97	5
3	14	6	164	31
4	23	15	193	93
5	31	22	227	182
6	51	46	279	257
7	84	84	318	323
8	101	107	358	348
9	112	135	389	363
10	121	164	414	375

Sample Timings (minutes) 5x2, 1x6, 4x20 as in Table 5.6

Table 5.12

Production of carbon monoxide from G_7

Sample T°C	222.3	248.5	277.0	300.9
1	0	0	245	1
2	3	9	396	35
3	10	22	459	126
4	16	46	463	313
5	22	76	506	415
6	40	137	540	483
7	80	208	581	576
8	101	237	614	616
9	115	254	641	643
10	127	279	653	671

Sample Timings as in Table 5.11

Table 5.13

Production of carbon monoxide from β-Schardinger dextrin

T°C / Sample	249.9	277.7	300.3
1	0	} 4	} 1
2	0		
3	0	7	2
4	0	12	25
5	0	20	69
6	0	37	139
7	0	101	296
8	0	149	361
9	0	201	401
10	0	291	427

Sample Timings as in Table 5.6

Table 5.14

Production of carbon monoxide from amylose

T°C / Sample	222.3	248.0	275.7	300.3
1	0	0	0	0
2	0	2	3	6
3	1	6	10	13
4	2	10	17	19
5	2	14	28	26
6	2	18	52	48
7	5	27	106	102
8	5	33	144	155
9	5	34	194	183
10	5	48	265	202

Sample Timings as in Table 5.9

Table 5.15

Production of carbon monoxide from retrograded amylose

Sample / T°C	248.0	277.5	300.5
1	1	1	1
2			
3		4	2
4	3		10
5		5	36
6	4	9	94
7	7	21	204
8	10	42	238
9	12	60	261
10	16	81	278

Sample Timings as in Table 5.6

Table 5.16

Production of carbon monoxide from starch

Sample / T°C	248.6	277.7	301.5
1	1	1	2
2	2		
3		2	2
4	3	4	10
5		10	89
6	3	37	198
7	5	94	280
8	11	130	308
9	25	160	333
10	45	186	360

Sample Timings as in Table 5.6

Table 5.17

Production of carbon monoxide from amylopectin

Sample \ T°C	248.8	277.6	299.0
1	0	} 1	} 2
2	0		
3	} 2	4	5
4		7	25
5	2	15	72
6	4	48	169
7	11	105	286
8	20	141	320
9	30	170	348
10	40	248	368

Sample Timings as in Table 5.6

Table 5.18

Production of carbon monoxide from dextran

Sample \ T°C	249.3	277.5	299.0
1	0	0	1
2	1	6	3
3	1	18	9
4	3	36	48
5	4	54	104
6	9	94	184
7	23	159	296
8	30	222	331
9	39	285	359
10	53	336	384

Sample Timings as in Table 5.6

Table 5.19

Production of carbon dioxide from glucose

Sample \ T°C	222.3	248.7	277.0	300.3
1	1	6	73	41
2	3	178	126	142
3	7	230	215	196
4	11	261	242	238
5	22	291	265	269
6	47	330	300	298
7	79	364	340	340
8	96	381	361	361
9	108	398	390	384
10	116	414	409	403

Sample Timings as in Table 5.6

Table 5.20

Production of carbon dioxide from maltose

Sample \ T°C	222.3	248.3	277.7	299.4
1	0	110	130	145
2	0	269	235	275
3	2	346	289	369
4	3	394	324	467
5	7	452	366	542
6	25	534	427	621
7	66	622	517	708
8	84	655	568	749
9	96	691	610	793
10	106	729	648	837

Sample Timings as in Table 5.6

Table 5.21

Production of carbon dioxide from G_3

Sample / T°C	222.3	248.2	277.0	301.0
1	79	88	101	262
2	203	334	228	431
3	295	480	297	636
4	353	561	335	738
5	397	649	381	816
6	468	760	454	895
7	526	853	561	996
8	558	898	626	1058
9	589	938	690	1105
10	607	981	752	1155

Sample Timings as in Table 5.8

Table 5.22

Production of carbon dioxide from G_4

Sample / T°C	222.3	248.3	272.0	299.1
1	102	165	303	248
2	278	461	498	448
3	366	569	567	543
4	432	631	611	643
5	471	704	661	712
6	545	795	739	783
7	589	870	838	852
8	623	908	894	900
9	643	945	945	955
10	661	976	998	1006

Sample Timings as in Table 5.9

Table 5.23

Production of carbon dioxide from G_5

Sample \ T°C	222.3	249.3	277.0	299.6
1	145	28	250	209
2	219	121	639	559
3	277	242	800	691
4	318	287	881	849
5	371	379	958	990
6	460	504	1076	1131
7	501	612	1212	1300
8	535	666	1294	1401
9	570	709	1371	1502
10	602	749	1440	1599

Sample Timings as in Table 5.10

Table 5.24

Production of carbon dioxide from G_6

Sample \ T°C	222.3	248.5	277.7	299.6
1	13	18	200	0
2	62	43	378	93
3	97	73	466	245
4	126	97	507	402
5	148	137	527	574
6	192	203	604	810
7	251	260	688	1003
8	278	309	733	1068
9	293	380	787	1129
10	306	432	837	1177

Sample Timings as in Table 5.11

Table 5.25

Production of carbon dioxide from G_7

Sample	T°C 222.3	248.5	277.0	300.9
1	6	14	342	10
2	34	84	494	200
3	65	147	596	516
4	93	199	656	716
5	113	278	714	845
6	162	422	983	969
7	242	545	1124	1153
8	276	604	1199	1250
9	300	662	1272	1337
10	316	713	1372	1410

Sample Timings as in Table 5.11

Table 5.26

Production of carbon dioxide from β-Schardinger dextrin

Sample	T°C 249.9	277.7	300.3
1	0	1	1
2	1	5	1
3	1	10	7
4	2	16	29
5	3	28	77
6	3	67	183
7	4	196	449
8	5	320	604
9	6	463	693
10	9	542	761

Sample Timings as in Table 5.6

Table 5.27

Production of carbon dioxide from amylose

Sample / T°C	222.3	248.0	275.7	300.3
1	0	6	8	2
2	0	6	13	6
3	0	11	21	19
4	1	13	27	48
5	2	14	38	157
6	3	19	65	273
7	6	20	115	596
8	8	21	164	717
9	11	23	260	794
10	13	36	311	842

Sample Timings as in Table 5.9

Table 5.28

Production of carbon dioxide from retrograded amylose

Sample / T°C	248.0	277.5	300.5
1	1	1	2
2	2	4	5
3	3	7	13
4	4	9	35
5	6	15	87
6	9	29	181
7	16	64	419
8	20	103	501
9	25	164	548
10	32	231	561

Sample Timings as in Table 5.6

Table 5.29

Production of carbon dioxide from starch

Sample \ T°C	248.6	277.7	301.5
1	0	5	4
2	1	6	4
3	2	10	5
4	2	16	32
5	3	40	232
6	5	109	496
7	28	249	668
8	84	313	736
9	177	367	800
10	258	407	852

Sample Timings as in Table 5.6

Table 5.30

Production of carbon dioxide from amylopectin

Sample \ T°C	248.8	277.6	299.0
1	1	15	1
2	3	27	6
3	5	46	14
4	6	59	41
5	8	94	129
6	12	202	337
7	25	346	608
8	37	419	667
9	51	481	724
10	66	535	764

Sample Timings as in Table 5.6

Table 5.31

Production of carbon dioxide from dextran

Sample \ T°C	249.3	277.5	299.0
1	1	9	1
2	11	29	12
3	17	49	45
4	21	65	128
5	28	97	282
6	39	183	522
7	64	391	810
8	79	603	929
9	97	776	1018
10	123	898	1085

Sample Timings as in Table 5.6

Table 5.32

Production of water from glucose

Sample \ T°C	222.3	248.7	277.0	300.3
1	14	27	2805	1089
2	270	4127	3274	2216
3	1144	4573	3790	2503
4	1793	4708	3918	2736
5	2496	4846	4032	2842
6	3255	5002	4143	2928
7	3730	5170	4271	3026
8	3888	5240	4342	3070
9	4033	5305	4477	3113
10	4106	5367	4484	3156

Sample Timings as in Table 5.6

Table 5.33

Production of water from maltose

Sample	T°C 222.3	248.3	277.7	299.4
1	4	1257	3100	3660
2	11	3217	3936	4518
3	85	3910	4245	4890
4	300	4241	4404	5302
5	722	4543	4567	5603
6	1832	4889	4853	5853
7	3595	5212	5217	6100
8	4053	5315	5382	6197
9	4266	5454	5538	6283
10	4389	5567	5651	6366

Sample Timings as in Table 5.6

Table 5.34

Production of water from G_3

Sample \ T°C	222.3	248.2	277.0	301.0
1	1000	630	2170	2660
2	3499	3250	2636	3285
3	4428	4227	2878	4097
4	4848	4588	2986	4599
5	5068	4906	3111	4837
6	5406	5427	3300	5038
7	5737	5685	3558	5257
8	5849	5822	3678	5383
9	5950	5904	3779	5518
10	6018	6014	3875	5599

Sample Timings as in Table 5.8

Table 5.35

Production of Water from G_4

Sample \ T°C	222.3	248.3	272.0	299.1
1	906	850	2495	1980
2	2871	2642	3355	2860
3	3527	3177	3608	3195
4	3982	3415	3720	3521
5	4209	3639	3884	3694
6	4545	3899	4099	3844
7	4766	4117	4337	4052
8	4907	4193	4452	4140
9	4962	4270	4570	4223
10	5029	4352	4669	4296

Sample Timings as in Table 5.9

Table 5.36

Production of water from G_5

Sample \ T°C	222.3	249.3	277.0	299.6
1	1696	57	1006	1425
2	2458	657	3621	3455
3	3012	1843	4328	3994
4	3389	2554	4613	4559
5	3745	3310	4854	4994
6	4253	4114	5164	5384
7	4655	4685	5535	5809
8	4830	4860	5698	5998
9	5072	4995	5856	6170
10	5419	5120	6023	6311

Sample Timings as in Table 5.10

Table 5.37

Production of water from G_6

Sample \ T°C	222.3	248.5	277.7	299.6
1	149	90	1285	0
2	944	464	2597	1025
3	1536	1048	2944	2325
4	1934	1551	3099	3323
5	2193	2211	3289	4164
6	2723	3082	3481	5155
7	3259	3162	3717	5889
8	3422	3538	3845	6044
9	3526	3951	3979	6158
10	3596	4322	4108	6253

Sample Timings as in Table 5.11

Table 5.38

Production of water from G_7

Sample \ T°C	222.3	248.5	277.0	300.9
1	36	112	3113	28
2	563	516	3604	1156
3	1064	1220	3892	3098
4	1480	1656	4024	3888
5	1730	2285	4155	4314
6	2308	3225	4512	4684
7	3083	3937	4860	5163
8	3347	4170	4999	5380
9	3519	4350	5107	5542
10	3612	4536	5190	5675

Sample Timings as in Table 5.11

Table 5.39

Production of water from β-Schardinger dextrin

Sample \ T°C	249.9	277.7	300.3
1	2	11	0
2	2	57	0
3	3	158	65
4	6	250	231
5	12	341	476
6	19	551	881
7	56	1065	1976
8	97	1651	2523
9	153	2330	2793
10	217	2654	2930

Sample Timings as in Table 5.6

Table 5.40

Production of water from amylose

Sample \ T°C	222.3	248.0	275.7	300.3
1	0	110	202	147
2	0	124	291	273
3	0	235	317	363
4	14	260	345	507
5	19	276	388	1083
6	29	322	516	1885
7	42	388	804	3695
8	66	450	1118	4183
9	79	539	1827	4397
10	114	646	3032	4503

Sample Timings as in Table 5.9

Table 5.41

Production of water from retrograded amylose

Sample \ T°C	248.0	277.5	300.5
1	3	0	0
2	11	7	0
3	21	15	37
4	34	37	215
5	41	82	610
6	56	164	1139
7	111	538	2174
8	141	952	2441
9	189	1402	2568
10	246	1909	2623

Sample Timings as in Table 5.6

Table 5.42

Production of Water from starch

Sample / T°C	248.6	277.7	301.5
1	5	49	7
2	10	67	9
3	19	101	9
4	23	222	259
5	28	536	1900
6	49	1318	3480
7	261	2919	3946
8	776	3338	4043
9	1671	3606	4199
10	2436	3794	4278

Sample Timings as in Table 5.6

Table 5.43

Production of water from amylopectin

Sample / T°C	248.8	277.6	299.0
1	0	73	0
2	6	198	12
3	9	506	38
4	10	935	223
5	17	1631	871
6	40	2878	2196
7	107	3833	3228
8	188	4199	3391
9	284	4426	3520
10	428	4600	3606

Sample Timings as in Table 5.6

Table 5.44

Production of water from dextran

Sample \ T°C	249.3	277.5	299.0
1	13	308	28
2	42	437	131
3	66	579	299
4	84	709	817
5	123	869	1679
6	188	1323	2889
7	275	2685	4449
8	447	3777	4798
9	496	4881	4979
10	624	5552	5110

Timings as in Table 5.6

Table 5.45

Production Ratios of Water:Carbon Dioxide:Carbon Monoxide

Compound	ca 225°C	ca 250°C	ca 275°C	ca 300°C
Glucose	110 : 3 : 1	80 : 5 : 1	50 : 3 : 1	30 : 3 : 1
Maltose	70 : 4 : 1	70 : 5 : 1	30 : 3 : 1	50 : 3 : 1
G_3	40 : 3 : 1	40 : 5 : 1	20 : 2 : 1	20 : 3 : 1
G_4	20 : 3 : 1	15 : 3 : 1	15 : 3 : 1	10 : 2 : 1
G_5	25 : 3 : 1	20 : 3 : 1	20 : 4 : 1	15 : 3 : 1
G_6	40 : 3 : 1	20 : 3 : 1	10 : 2 : 1	15 : 2 : 1
G_7	40 : 3 : 1	20 : 3 : 1	10 : 2 : 1	10 : 2 : 1
β-Schardinger Dextrin	n.d.[1]	n.d.	10 : 2 : 1	5 : 2 : 1
Amylose	n.d.	n.d.	30 : 3 : 1	30 : 4 : 1
Retrograded Amylose	n.d.	n.d.	25 : 3 : 1	10 : 2 : 1
Starch	n.d.	n.d.	20 : 2 : 1	15 : 2 : 1
Amylopectin	n.d.	n.d.	35 : 3 : 1	15 : 2 : 1
Dextran	n.d.	n.d.	15 : 3 : 1	15 : 3 : 1

1) n.d. = not determined

Table 5.46

Rates of Production of Carbon Monoxide[1)]

Sample / T°C ca.	225	250	275	300
Glucose	3	9	19	22
Maltose	1	17	25	45
G_3	8	19	75	75
G_4	11	35	54	102
G_5	7	10	49	83
G_6	3	4	56	34
G_7	2	12	213	98
β-Schardinger Dextrin	n.d.[2)]	0	4	12
Amylose	0.1	2	4	8
Retrograded Amylose	n.d.	0.6	1	7
Starch	n.d.	0.4	3	17
Amylopectin	n.d.	0.4	4	14
Dextran	n.d.	1	9	18

1) Units are moles x 10^6/g/min

2) n.d. = not determined

Table 5.47

Rates of Production of Carbon Dioxide[1)]

Sample / T°C ca.	225	250	275	300
Glucose	3	68	68	130
Maltose	2	112	100	258
G_3	48	160	105	330
G_4	61	200	257	465
G_5	45	69	262	475
G_6	16	24	150	150
G_7	11	48	227	325
β-Schardinger Dextrin	n.d.[2)]	0.3	6	15
Amylose	0.1	2	8	22
Retrograded Amylose	n.d.	2	3	15

Table 5.47 (cont.)

Starch	n.d.	2	9	41
Amylopectin	n.d.	0.4	15	27
Dextran	n.d.	5	17	47

1) Units are moles x 10^6/g/min

2) n.d. = not determined

Table 5.48

Rates of Production of Water[1)]

Sample	225	250	275	300
Glucose	360	1900	1900	1900
Maltose	150	1030	1575	3250
G_3	570	1075	1075	3000
G_4	690	1175	1600	2700
G_5	540	580	1650	3000
G_6	260	375	1125	1650
G_7	176	390	1500	1500
β-Schardinger Dextrin	n.d.[2)]	25	63	76
Amylose	0.1	70	140	266
Retrograded Amylose	n.d.	7	17	100
Starch	n.d.	13	110	350
Amylopectin	n.d.	30	270	177
Dextran	n.d.	20	170	270

1) Units are moles x 10^6/g/min

2) n.d. = not determined

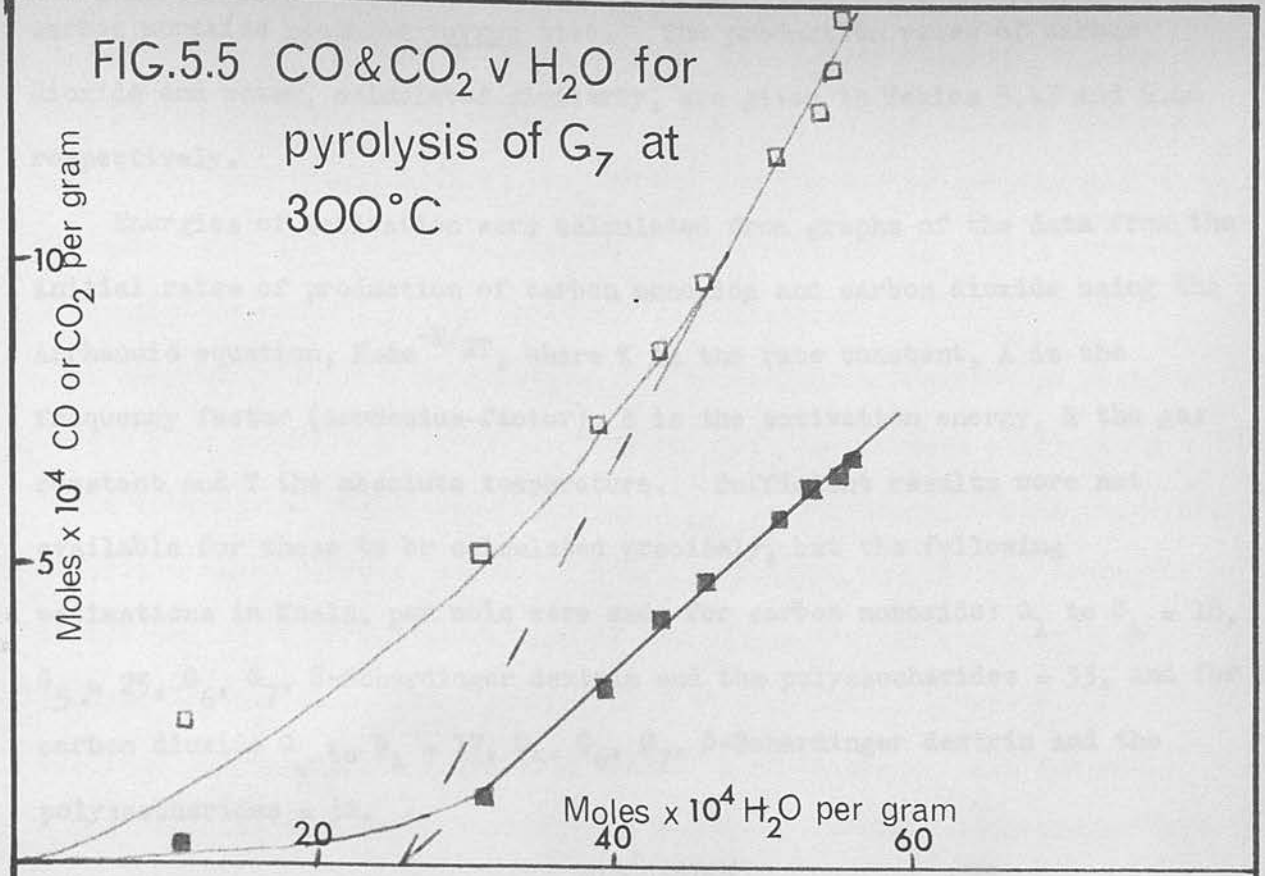


FIG.5.5 CO & CO_2 v H_2O for pyrolysis of G_7 at 300°C

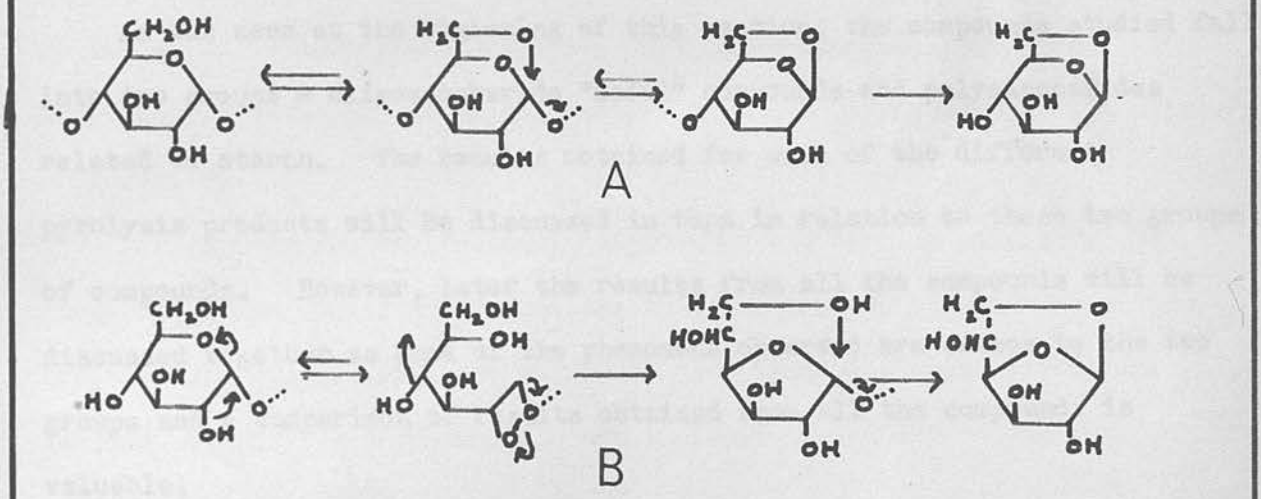


FIG.5.6 Formation of A anhydroglucopyranose and B anhydroglucofuranose

carbon monoxide produced versus time. The production rates of carbon dioxide and water, calculated similarly, are given in Tables 5.47 and 5.48 respectively.

Energies of activation were calculated from graphs of the data from the initial rates of production of carbon monoxide and carbon dioxide using the Arrhenuis equation, $K=Ae^{-E/RT}$, where K is the rate constant, A is the frequency factor (Arrhenius factor), E is the activation energy, R the gas constant and T the absolute temperature. Sufficient results were not available for those to be calculated precisely, but the following estimations in Kcals. per mole were made for carbon monoxide: G_1 to G_4 = 18, G_5 = 25, G_6, G_7, β-Schardinger dextrin and the polysaccharides = 33, and for carbon dioxide G_1 to G_4 = 17, G_5, G_6, G_7, β-Schardinger dextrin and the polysaccharides = 32.

DISCUSSION

As was seen at the beginning of this section, the compounds studied fall into two groups - oligosaccharide "model" compounds and polysaccharides related to starch. The results obtained for each of the different pyrolysis products will be discussed in turn in relation to these two groups of compounds. However, later the results from all the compounds will be discussed together as some of the phenomena observed are common to the two groups and a comparison of results obtained from all the compounds is valuable.

The 'Char' Fraction

The residual weights of the compounds on pyrolysis, accurate to ±1%, expressed as percentages of dry-weight of the starting material, are shown in Table 5.3. It may be seen that, for the oligosaccharides at 222°C, the residual weight increases with increasing chainlength, indicating that the

thermal stability is also increasing. At the higher temperatures, however, this is not the case. For example at 300°C the residual weight increases with increasing chainlength only up to G_5, and thereafter the residual weight decreases with increasing chainlength. This reversal is also apparent, although less marked, at the intermediate temperatures.

Samples of shorter chainlength show a continuous decrease in residual weight with increase of pyrolysis temperature, the decrease approaching a limit towards the higher temperatures. The longer-chain samples, however, exhibit a sharp decrease in residual weight between the heating temperatures of 250 and 275°C. The appearance of the polysaccharide residues also changes in this temperature range from that of slightly brown-coloured modified polysaccharide samples to that of a black char. All the small sugar residues were black chars. The behaviour of the β-Schardinger dextrin is of especial interest, since it is an oligosaccharide with no end-groups. At 250°C, it is more stable than even the polysaccharides; at higher temperatures, however, it is less stable than the corresponding open-chain oligomer, G_7.

Trends shown by the residual weights for the various samples at different temperatures would indicate that the mode of degradation of the longer-chain samples might be different from that of the shorter-chain samples, especially above 249°C. This result may be due to the influence of end-groups.

Previous workers (Bryce and Greenwood, 1966a) have found that, although the differences are small, amylopectin is relatively more stable than amylose. Although the results shown here agree with this trend, it is thought that the differences are too small to be considered significant. Indeed, it is suggested that molecular size is more important than the type

of glycosidic linkage in determining the resistance of a saccharide to prolonged heating.

The difference between the thermal breakdown of oligosaccharides up to G_4 and that of saccharides of chainlength 5 or greater is further emphasized by the molar ratios of carbon, hydrogen and oxygen in the chars (see Table 5.4). Small sugars exhibit very little variation of this ratio with temperature, whilst there is a definite increase both of carbon and of hydrogen with respect to oxygen for the chars obtained from the pyrolysis of G_5 and larger saccharides. Amylose, the only substance for which the chars from all four pyrolysis temperatures were available in sufficient quantity for analysis, demonstrates very clearly this increase of carbon and hydrogen with respect to oxygen.

From an analysis of rate plots obtained at pyrolysis temperatures between 150 and 240°C, Puddington (1948) postulated that the first stage in the degradation of glucose and maltose, but not of starch, was a simple dehydration reaction. The rather more direct evidence provided here by the chemical analysis of the chars demonstrates that this initial dehydration does not, in fact, occur in any of the saccharides studied.

The 'Syrup' Fraction

One of the largest, and therefore most important, products from the pyrolytic degradation of saccharides is the syrup fraction. The composition of this fraction has been found to provide some indication of the mode of degradation, and hence has been examined in detail.

The syrup obtained from the pyrolysis of glucose is composed to a large extent (50-60%) of glucose itself, i.e. an appreciable amount of the glucose sample has simply distilled out of the furnace vessel without degradation. This obviously affects the amounts of degradation products which are obtained

when a glucose sample is placed in the furnace and is one of the reasons that the behaviour of glucose differs from that of the higher homologues.

Up to 10% of the syrup fraction from the pyrolysis of maltose, and about 1% of that from the pyrolysis of maltotriose, consists of glucose. To produce glucose from the saccharides, glycosidic bonds must be broken and an unmodified glucose unit eliminated. As the breaking of only one glycosidic bond is involved in the elimination of a terminal unit, it is more likely that the glucose is produced from a chain-end. As the chainlength increases, therefore, the chance of an unmodified glucose molecule being produced, and distilling out without degradation, correspondingly decreases. It is not surprising, therefore, that the amount of glucose in the syrups decreases so rapidly with increasing chainlength of the pyrolysis sample, the syrups obtained from samples of chainlength greater than 3 having zero glucose content. The presence of glucose in pyrolysis distillates from glucose, maltose and maltotriose has not previously been reported. That it has been detected here is probably due partly to the high sensitivity of the glucose assay, and partly to the apparatus used, in which conditions are particularly favourable for the rapid removal of products from the reaction zone.

The chromatograms obtained from the TMS ethers of the syrups (see Figures 5.3 and 5.4) again demonstrated that only oligomers of six or more glucose units degrade in the same way as the polysaccharides i.e. the syrups from the small oligomers contain a complex mixture of substances, while those from the larger samples are predominantly 1,6-anhydro-β-D-glucopyranose and 1,6-anhydro-β-D-glucofuranose. It might therefore appear that these small sugars may not be regarded as true "model" compounds for studies of the thermal degradation of starch.

The chromatograms of the TMS derivatives of the syrups obtained from G_6,

G_7, β-Schardinger dextrin and the polysaccharides were all of the same general pattern as those obtained by Sawardeker, Sloneker and Dimler (1965) from the syrups of waxy maize starch and dextran. The small, unidentified fraction may contain furfural, which was identified in the syrups of potato starch and its components by Bryce and Greenwood (1963b). Apart from this very small fraction, these syrups are composed entirely of 1,6-anhydroglucose, the relative amounts of the pyranose and furanose forms varying with the conditions of pyrolysis and the substance pyrolyzed. Dimler et al. (1965) found that no anhydrofuranose and 12% anhydropyranose was formed when the starch heated had a moisture content of 1.81%. Dried starch, however, yielded 0.9% of furanose and 19% pyranose, equivalent to a pyranose: furanose ratio of 21:1. While these results are interesting, actual values cannot be compared with those obtained here as the experimental conditions employed by Dimler are very different.

Under the conditions described above, it was found that the pyranose: furanose ratio for each substance was independent of pyrolysis temperature. These ratios, quoted in Table 5.5, are similar for the saccharides linked by 1→4 glycosidic bonds only. The relative amount of furanose in the syrup increases with the amount of 1→6 glycosidic linkages introduced into the 1→4 chain. It seems likely that the pyranose: furanose ratio is related to the number of tri-functionally-linked residues in the molecule. Thus the value of this ratio for amylopectin (with approx. 4% 1→6 links) and dextran (with approx. 4% 1→4 links) are similar.

It has been suggested (Gardiner, 1966) that anhydro-end-groups are formed in amylose by direct attack on a glycosidic bond by the primary hydroxyl group of the D-glucopyranose unit as shown in Figure 5.6A Scission of the glycosidic bond at C_4 of that unit would then produce 1,6-anhydroglucopyranose.

Formation of the furanose would require the glycosidic bond at C_4 to be broken before anhydro-formation in order that rearrangement of the pyranose ring into the furanose form might take place. This is shown in Figure 5.6.B.

Clearly, formation of anhydroglucose units from a long-chain glucan must occur by the breaking of a glycosidic bond and the liberation of an anhydroglucose unit from the end of the chain. It is to be noted that more chain ends may be produced by random scission of glycosidic bonds. An analogy might be drawn with some synthetic polymers which thermally degrade by an unzipping action to produce monomer only (Madorsky, 1964). It might be that the glucose unit at the non-reducing end is eliminated after attack on the glycosidic bond by the primary hydroxyl, forming anhydroglucose. The new end unit could then be eliminated, and so on, producing an unzipping effect. A similar unzipping mechanism from the reducing end would require initial formation of an anhydro-end-group i.e. initially a two-stage reaction.

Clearly, the large number of products obtained on pyrolysis of simple saccharides can only be produced by a variety of competing degradation reactions. The yields obtained of anhydroglucose are, however, so much greater than those of any other substance, that it seems probable that some sort of unzipping action might be one of the predominant reactions. The formation of anhydrofuranose means that at least some of the anhydroglucose is eliminated from the non-reducing end of the chain. The decrease of the anhydropyranose: anhydrofuranose ratio in the syrups with the increase in the number of branch-points in the chain could then be due to an interruption of the unzipping mechanism at the branch-points. The presence of glucose in the syrups from the smaller sugars would indicate that anhydroformation at the reducing end was, if not non-existent, at least limited.

Further support for the occurrence of an unzipping mechanism, probably

from the non-reducing end, was obtained from analysis of the syrup from the pyrolysis at 250°C of β-methylmaltoside. This syrup did not contain a complex mixture of substances, as did that of maltose, but consisted predominantly of β-methylglucoside and anhydroglucose. This is the result which would be expected if an unzipping action from the non-reducing end had occurred.

More information about the effect of end-groups on the thermal degradation is obviously required, and an extension of the above result to a complete study of the pyrolysis of the series of oligosaccharides with the reducing end blocked by, say, a methyl group should yield valuable information. A knowledge of the amounts of anhydroglucose produced with time of pyrolysis should also be helpful.

Major Volatile Products

Production of carbon monoxide, carbon dioxide and water: Typical graphs of the production of carbon monoxide, carbon dioxide and water with time of pyrolysis are shown in Figures 5.7, 5.8 and 5.9. In no instance was a sigmoidal-type curve obtained implying that there is no induction period, autocatalysis or liquid phase present in the thermal degradation of any of the samples studied. Similar results have been obtained for potato starch (Puddington, 1948) and for its components (Bryce and Greenwood, 1966a).

It may be seen from Tables 5.6 to 5.44 that, throughout the range studied, as the pyrolysis temperature increased there was a consistent increase in the quantity of carbon monoxide produced from all samples, and in the quantities of carbon dioxide and water produced from samples of chainlength 5 or more. There appears to be no definite relation between pyrolysis temperature and the amounts of carbon dioxide and water produced from the smaller molecules.

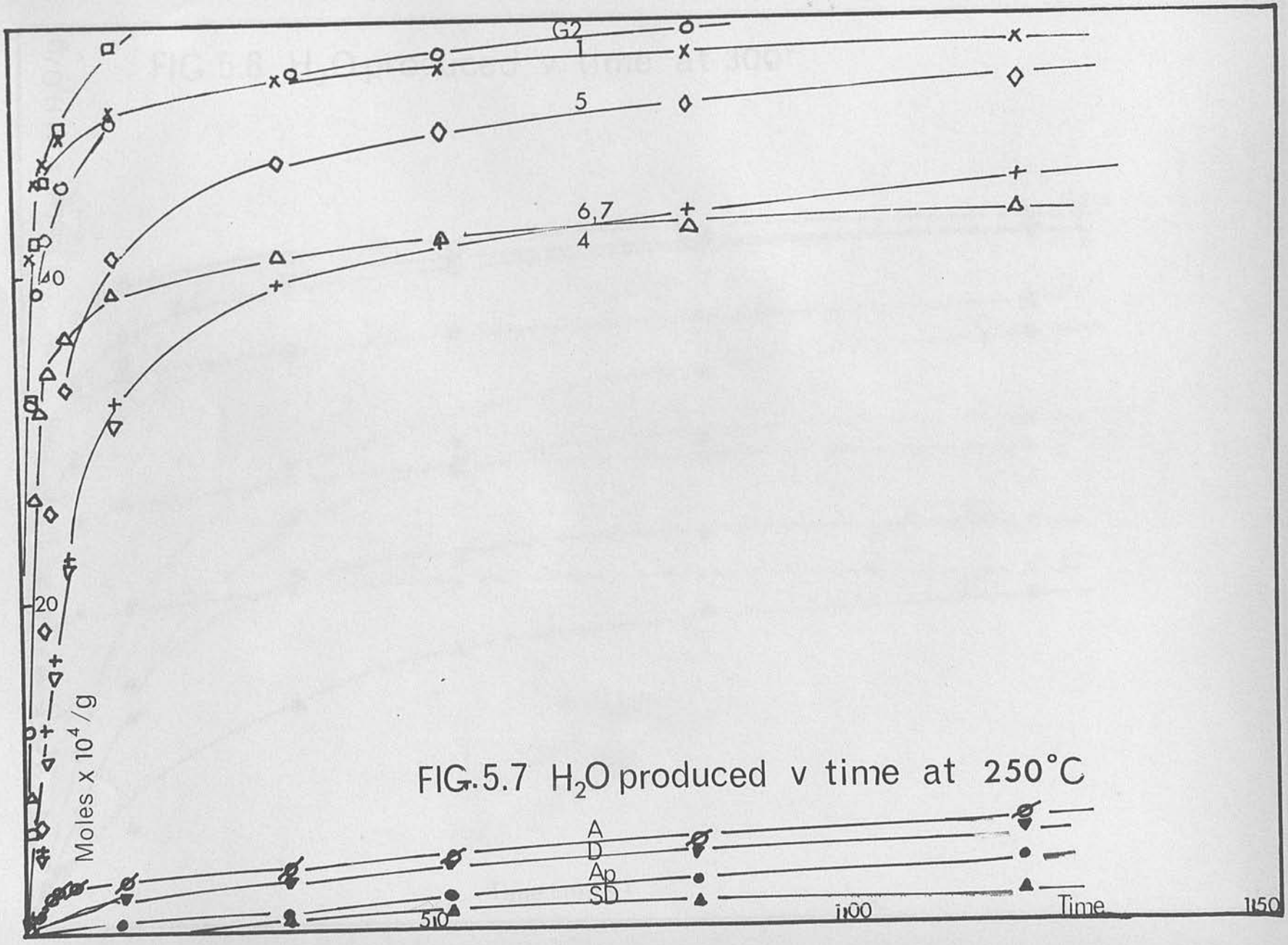


FIG. 5.7 H_2O produced v time at 250°C

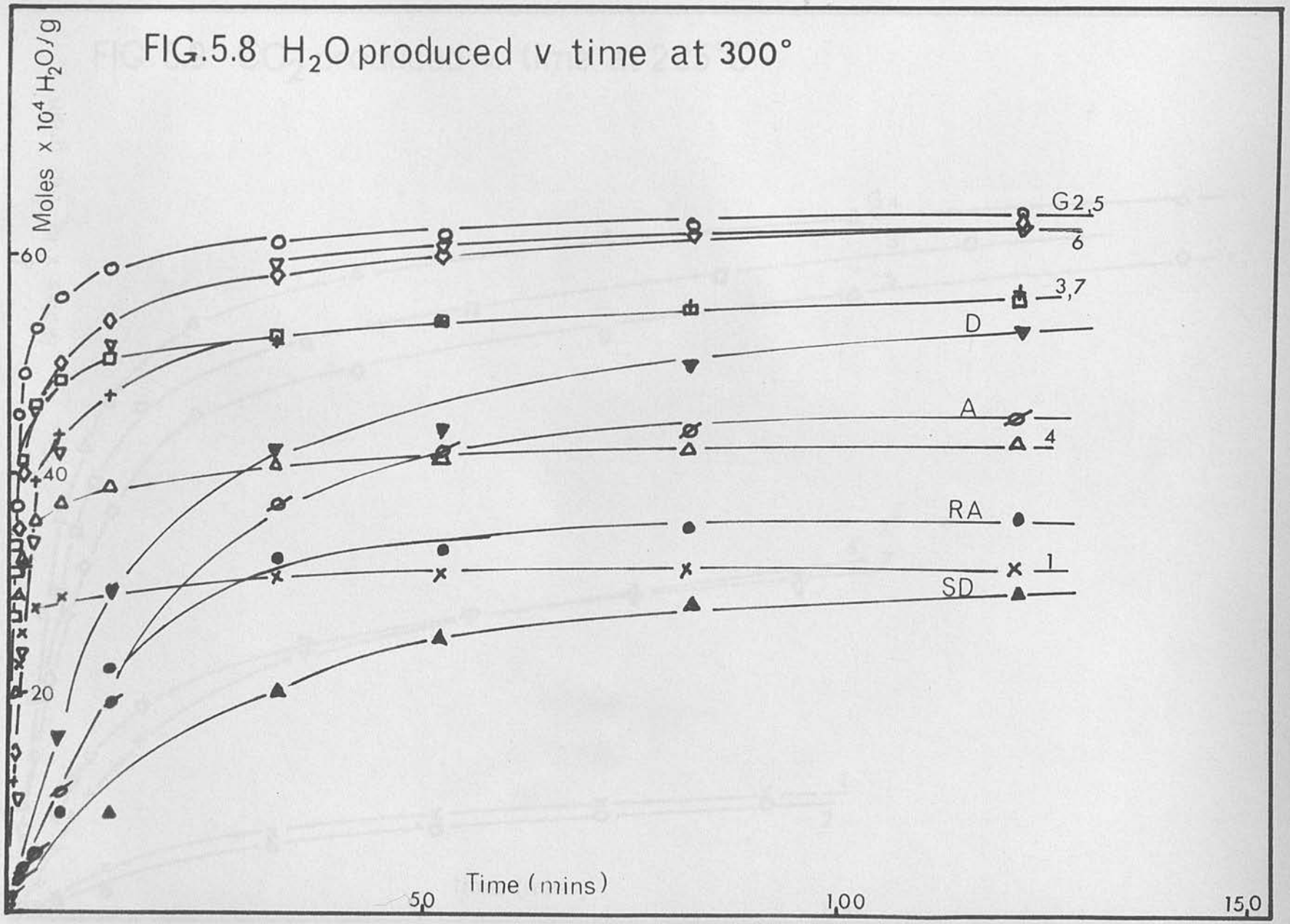


FIG.5.8 H_2O produced v time at 300°
Moles x 10^4 H_2O/g
60
40
20
G2,5
6
3,7
D
A
4
RA
1
SD
Time (mins)
5,0
1,00
15,0

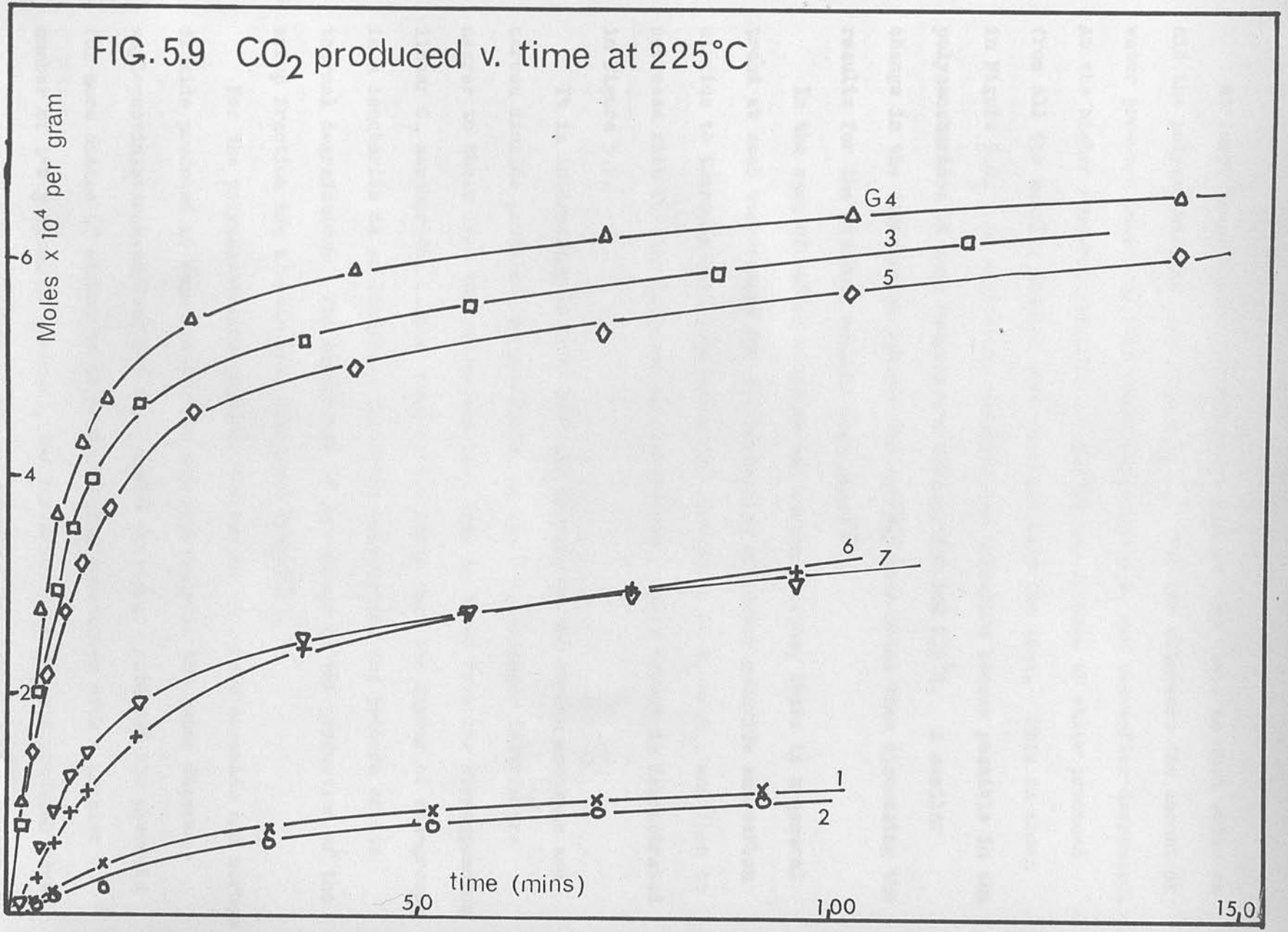


FIG. 5.9 CO_2 produced v. time at 225°C
Moles x 10^4 per gram
6
4
2
G 4
3
5
6
7
1
2
time (mins)
5,0
1,00
15,0

At lower temperatures the oligomers yielded ten times as much water as did the polysaccharides (see Figure 5.7). For the oligomers the amount of water produced increased with chainlength up to G_3 and thereafter decreased. At the higher temperatures (275 and 300°C) the amounts of water produced from all the samples studied were approximately the same. This is shown in Figure 5.8. An additional reaction may therefore become possible in the polysaccharides at some temperature between 250 and 275°C. A similar change in the degradation pattern has already been noted when discussing the results for the residual weights (see page 88).

In the case of carbon monoxide and carbon dioxide, there is a general trend at each temperature for the production of carbon monoxide and carbon dioxide to increase with increasing chainlength up to G_4 or G_5, and then to decrease with further increase in chainlength. This effect is demonstrated in Figure 5.9.

It is interesting to note that the amounts of the carbon monoxide and carbon dioxide produced, on pyrolysis, by the β-Schardinger dextrin are nearer to those from the polysaccharides than to those from the corresponding linear G_7 saccharide. This result would imply that the number of end-groups in a saccharide is an important factor in determining the pattern of its thermal degradation. The importance of end-groups in the production of the syrup fraction has already been discussed (page 92).

For the polysaccharides studied, the amount of carbon monoxide and carbon dioxide produced at each temperature was generally in the order dextran > amylopectin > starch > amylose and retrograded amylose. Although the trend is for more oxides of carbon to be produced from substances with a greater number of 1→6 glycosidic linkages, the differences in amounts produced were not great enough for this to be the only determining factor. The amount of

water produced with time was approximately the same for all the polysaccharides pyrolyzed.

It has been suggested that water is formed in several ways (Bryce and Greenwood, 1966a), including the removal of residual, bound water. By plotting carbon monoxide and carbon dioxide versus water produced at a given temperature a curve, such as that shown in Figure 5.5, is obtained. In all cases the production of carbon monoxide and carbon dioxide becomes - within experimental error - a direct function of the evolved water. The resultant linear relation extrapolates to the origin for the polysaccharides at low temperatures. For the polysaccharides at the higher temperatures, however, and for the small sugars at all temperatures, extrapolation of the straight-line portion yielded a positive intercept on the water axis. This positive quantity of water was taken by Bryce and Greenwood (1966a) to be a measure of the residual bound water, and the linear portion to represent the limiting ratios of degradation products. It would seem, however, that the system is rather more complex than this explanation suggests - it is unlikely that there is no bound water eliminated at 250°C, but an appreciable amount at higher temperatures.

Bryce and Greenwood (1966a) found that general decomposition and dextrinization occurs in starch about 220°C. The results reported in this section are in agreement with this claim, but indicate that such decomposition is limited. In the DTA studies of these polysaccharides (Section 3) it was found that the first major indication of chemical reaction was noted at 280-300°C. Allowing for the discrepancy in temperature brought about by the use of a dynamic method in the measurement, this effect might be equivalent to the occurrence of a further chemical reaction in the temperature range 250-275°C.

The indications are, therefore, that this intercept on the water-production axis, rather than representing desorption of bound water, further supports the view already put forward (see page 88) that more drastic chemical decomposition occurs between 250 and 275°C. It is thus possible to infer that pyrolysis involves distinctly different processes from dextrinization.

The limiting ratios of water:carbon dioxide:carbon monoxide are shown in Table 5.45. Although the amount of water is subject to variation, the carbon dioxide:carbon monoxide ratios are fairly constant throughout the pyrolyses and are generally in agreement with that of 3:1 reported by Puddington (1948) and Bryce and Greenwood (1966a).

Rates of Production and Activation Energies: The rates of production of carbon monoxide, carbon dioxide and water, shown in Tables 5.46, 5.47 and 5.48 respectively, reflect the dependence of the thermal degradation on molecular size, type of glycosidic bonds and pyrolysis temperature, which has been discussed above.

In every case, the rate of production of water is very much greater than that of either carbon monoxide or carbon dioxide. It is generally recognized that the evolution of water is a complex process involving more than one reaction. This has already been discussed above. For this reason, an energy of activation was not calculated from the results for the rates of production of water.

In such a complicated system, it is likely that a large number of competing reactions are occurring simultaneously, and it is feasible that carbon monoxide and carbon dioxide may also be produced by more than one reaction. With this proviso, however, activation energies were calculated for the production of carbon monoxide and carbon dioxide.

Bryce (1964) found values for the activation energy of thermal degradation

of 20 Kcal. per mole for glucose, isomaltose, maltose and maltotriose, and 29 Kcal. per mole for potato starch and its components. Puddington (1948) also reported a value of 29 Kcal. per mole for potato starch, but obtained figures of 29 and 35 Kcal. per mole for glucose and maltose respectively. The results shown on page 87 are in general agreement with these values.

Two points of interest arise from the values of the activation energies. Firstly, for each substance the activation energies for the production of carbon monoxide and carbon dioxide are the same. Whilst this might be purely chance, it could mean that they are produced by the same reaction. In any case, it would be expected that their production would follow the same pattern. That this does happen has already been shown in the previous subsection. Secondly, the activation energies fall into two distinct groups - G_1 to G_4, and the larger saccharides. This division into these two groups has been noted throughout the results and discussion.

Conclusions

It has been shown in this section that the mode of degradation of the smaller oligomers, G_1 to G_4 in the maltodextrin series, differs radically from that of the larger saccharides. Only molecules containing more than five glucose units can be considered as "model" compounds for studies of the thermal degradation of amylose. The results indicate that the relative proportion of reducing end-groups in a saccharide is an important factor in determining the pattern of its thermal degradation. It was found that there was no initial dehydration step in the degradation of any of the substances studied. Evidence has been put forward which suggests that the production of anhydroglucose occurs by an unzipping mechanism, probably from the non-reducing end. In the case of the polysaccharides, further chemical decomposition was found to occur between 250 and 275°C, implying that

pyrolysis is a process quite distinct from dextrinization.

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The Thermal Degradation of Starch

Part VII*). Differential Thermal Analysis of Maltodextrins and of Starch and its Components

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Introduction

Differential thermal analysis (DTA) is among the physicochemical techniques which have recently become generally available for studying thermal reactions. In this technique, the sample to be studied, or a mixture of the sample and a thermally-inert material such as calcinated kaolin or alumina, is heated at a uniform rate. The temperature of the sample, measured by thermocouples, is then compared with that of pure inert material heated in an identical manner. Any exothermic or endothermic reaction in the sample causes a positive or negative temperature difference between the sample and reference substance, and this is recorded, usually automatically, as a positive or negative „peak" on the resultant thermogram.

Several factors affect the thermogram and make any comparison of results obtained by different authors more difficult. For example, a fast rate of heating emphasises the difference in temperature between the sample and reference substances, and hence larger, sharper peaks are obtained than at slower heating rates. There is thus less chance of small peaks being missed. On the other hand, being a dynamic method, the higher the rate of heating, the greater the discrepancy between the actual and apparent temperatures of reaction. In practice, heating rates of between 10 and 20 °C per minute are generally used. The amount of sample, the way in which it is packed, and the design of the sample-holder can also affect the apparent reaction temperature and the height and width of the resultant peaks. Moreover, it is rarely possible to obtain an ideal inert reference material, that is, one which undergoes no physical or chemical change on heating, and which has the same heat capacity and thermal characteristics as the sample under study. Experimental procedures for minimizing these variables on the thermograms have been put forward (1), and, in particular, a controlled atmosphere during the thermal analysis of organic materials has been recommended (2).

Differential thermal analysis has been applied successfully to synthetic polymers (3) and to cellulose (4). However, there has not been a great deal of work reported for starch. Results obtained by various authors are shown in Table 1. The lack of agreement, although due in part to variation in technique and instrumentation as outlined above, can also be attributed to the treatment given to the starch. Many of the starches used are characterized poorly, or not at all; in some cases not even the botanical source is given. The variation in drying of the starch is reflected by the size of the endotherm at ~ 120 °C, and it is questionable if this endotherm has any significance other than as a measure of the extent of drying of the sample. On this basis, although the drying procedures used by the authors in Table 1 differed, in no case was the sample adequately dried. Another variable is the atmosphere under which these analyses have been carried out, some being done in air and some in a nitrogen atmosphere.

Table 1
Differential Thermal Analysis Results

Starch	Endotherms [1])	Exotherms [1])	Ref.
?	175 °(s) 280°(s)	325 °(ms)	5
?	210 °(s) 320 °(ms)	510 °(m)	6
Rice	110 °(m) 260 °(vs) 295 °(vs)	365 °(s) 480 °(ms)	7
Maize	130 °(m) 280—310 °(s)	330—370 °(ms) 475 °(ms) 525 °(m)	7
Potato	125 °(m) 275—305 °(s)	410—500 °(m)	7
Pea	155 °(m) 260 °(ms) 290 °(s)	460—525 °(m)	7
?	115 °(s)	600 °(s)	8

[1]) Temperatures in °C.
(s) = small; (m) = medium; (vs) = very small; (ms) = medium small.

Oxidation will obviously affect the shape of the thermogram. However, when nitrogen is used, the atmosphere may not be completely inert throughout the run, as the nitrogen may be replaced by the evolved gases. Lastly, some of these results have been obtained by the „compressed sandwich packing" method in which the starch was in contact with „thermally inert" alumina, and it has been reported that salts affect the thermal degradation of starch (9). Morita admitted (7) that the use of alumina packing altered the thermograms, but continued to use this technique as he found that irreproduceable results were otherwise obtained.

The starch components have also been examined, but the limitations which apply to the studies on starch are also valid here. Morita (7) made a qualified distinction between the components from starches of certain botanical species such as potato. When the samples were analysed in a nitrogen atmosphere, he found that the amylopectin was characterized by two endotherms at 230 °C and 270 °C, while the amylose had one endotherm at 295 °C. Chesters and Thompson (10) reported differences in the exothermic reactions of the components in air above 330 °C. In addition, these authors suggested that amylose is more thermally stable than amylopectin.

We have attempted, therefore, to study a number of well-characterized starches and their components under uniform DTA conditions in order to obtain a critical evaluation of its use. In particular, we have considered:

1. the effect of salts on the DTA of starch;
2. the thermograms of common starches to see how they differ;
3. the differences between the thermograms of the amylose and amylopectin components of a starch;

*) Part VI: Applied Polymer Symposia, **2** (1966), 159

4. how the percentage of amylose in a starch affects the thermogram.

At the same time, a study has been made of the effect on the thermal stability of the increase in size of the oligomer series G_1 to G_7[1])

Experimental

Materials Used

The starches were isolated in these laboratories from the appropriate botanical source (11, 12). Potato and wheat starch were fractionated into their components, amylose and amylopectin, as previously described (11). Characteristics of the starches were:

Potato amylose:
$[\eta]$ in 0.15 M KOH = 240, c in g/ml; β-limit = 97 % conversion into maltose; iodine affinity = 20.0 %;

Potato amylopectin:
$[\eta]$ = 160; β-limit = 56; iodine affinity = 0.2;

Wheat amylose:
$[\eta]$ = 330; β-limit = 72; iodine affinity = 19.8;

Wheat amylopectin:
$[\eta]$ = 150; β-limit = 54; iodine affinity = 0.6.

A series of maltodextrins $G_3 - G_7$ was prepared by acid hydrolysis of amylose, and the paper chromatographic separation of the hydrolysate. The final sugar products were chromatographically pure. Their preparation will be described in detail elsewhere (13), G_1 and G_2 were commercial samples.

DTA Apparatus and Procedure

All analyses were carried out using a Du Pont 900 Differential Thermal Analyzer. Sample and reference were contained in thin-walled soda-glass tubes placed in a silver block, which also housed a heater element at an equal distance from the two tubes. Samples of starch and its components were contained in tubes of 2 mm. external diameter, while tubes of 4 mm. external diameter were used for the small sugars. Only the sample under observation was packed into the tube; no „inert" material being added. A similar volume of glass beads was used as reference. The temperatures of sample and reference material were measured by thermocouples placed in the centre of each, and the difference in temperature was plotted as a function of sample-temperature on an X- Y recorder.

A heating rate of 20 °C/minute was used throughout this work. For a given sample, the temperatures obtained for peaks were usually found to be reproduceable to ± 2 °C. Complications could occur due to the evolution of gases, and loss of sample, which produce „noise" on the thermograms. Such a loss of sample results in the adoption of a higher baseline. However, it was found that by using a small starch sample — with a correspondingly small amount of gas being evolved — these anomalies were generally eliminated, and reproduceability attained.

As the heat of reaction is directly proportional to the amount of reacting substance, the peak area should be proportional to the mass of reacting sample. In practice, it was found that peak heights relative to the mass of sample used were not always the same. Although this was improved when care was taken to position the thermocouples in the centre of the sample, and to ensure optimum thermal contact between thermocouple, sample, and the walls of the sample holder, complete reproduceability in relative peak heights was not achieved. This could probably be attributed to disturbance of the system by evolution of gas on decomposition. Approximately 5 mg. samples were used for the small sugars and 2 mg. for starch samples.

In order to eliminate complications due to oxidation, and to ensure a similar atmosphere for the duration of the run, the analyses were carried out in vacuo with continuous pumping to remove evolved gases.

Results and Discussion

The interesting range of temperatures in the thermal degradation of a starch is that in which dextrinization takes place, and in which the evolution of gases begins. It was decided, therefore, to investigate the thermal behaviour at temperatures of up to 400 °C, with particular attention being paid to the range 250–350 °C.

Earlier workers have used the compressed sandwich packing technique. In this, the sample is packed between two layers of the „inert" material, such as alumina, but any effect the salt might have on the degradation of the starch has generally been ignored. Since we have found (9) that addition to starch of simple inorganic salts, such as sodium chloride, accelerates the thermal degradation as measured by the study of the evolved gases, the effect of alumina on DTA thermograms was investigated. Figure 1 shows the thermograms of potato starch alone, and mixed with 10 % aluminium oxide. It can be seen that, by addition of salt, the degradation pattern up to 287 °C was unaltered i.e. there was a small endotherm at 275 °C, a very small one at 282 °C, and an appreciable exotherm at 287 °C. Above this temperature, the pattern was completely altered; the large endotherm present at 302 °C was suppressed almost completely. An exactly similar effect on the thermogram was found when sodium chloride was mixed with the starch. It would appear, therefore, that the addition of a salt to a starch alters the DTA-thermogram completely, and so measurements should be made preferably with the starch sample only in

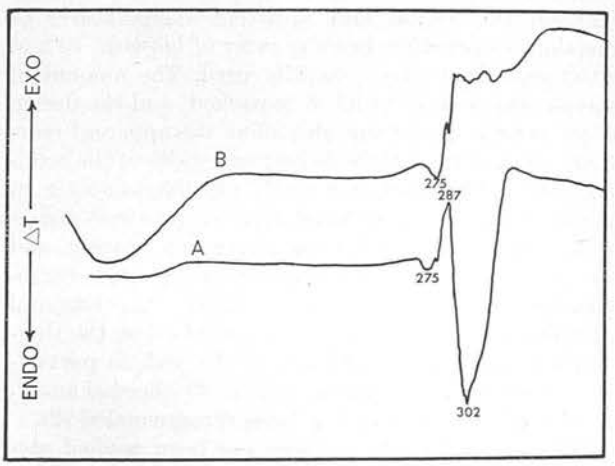

Fig. 1. Thermograms of (A) Potato starch alone, and (B) potato starch with 10 % aluminium oxide (Temperatures in °C.).

[1]) G_1 = glucose; G_2 = maltose; G_3 = maltotriose, etc.,

the tube. Reproduceable thermograms were then obtained, under the conditions described above, until well after the evolution of gas had begun.

Thermograms of Common Starches

Thermograms of potato, maize and wheat starches are shown in Figure 2. It can be seen that the general

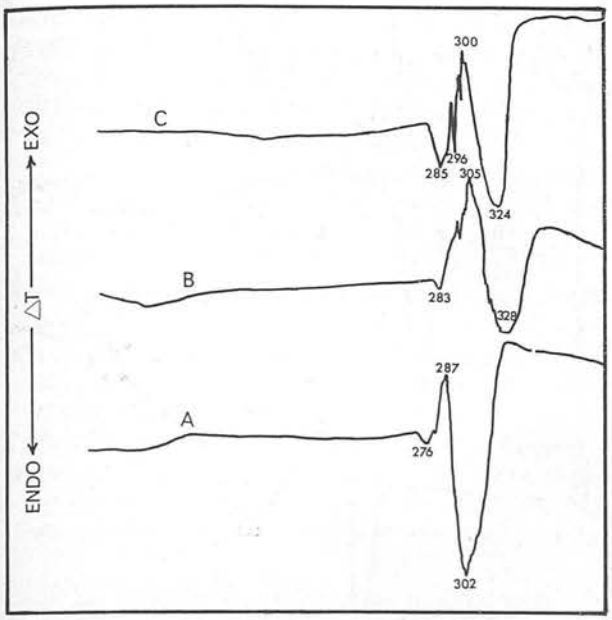

Fig. 2. Thermograms of (A) potato starch, (B) maize starch, and (C) wheat starch (Temperatures in °C).

pattern of each thermogram is the same; there is a small endothermic reaction at ca. 280 °C followed by an exotherm in the range 285—305 °C, and then a large endotherm in the range 302—330 °C. It was noticeable that potato starch was less stable than the two cereal starches, as shown by the fact that these characteristic temperatures occurred a few degrees lower than the corresponding ones for the cereal starches. The latter two starches behaved in a very comparable manner. Although the thermogram temperatures were reproduceable to ± 2 °C, the differences observed were not sufficiently large for different starches to be characterized.

Differences in thermal stability may be related to various factors, in which the granular structure and its inherent crystallinity are probably of more importance than the effect of differing thermal stabilities of amylose and amylopectin. This problem is discussed further below.

Thermograms of Amylose and Amylopectin

There are different ways of defining the thermal stability of a substance; sometimes this term is used to mean the threshold temperature i.e. the temperature at which decomposition starts, and sometimes resistance to prolonged heating. These need not necessarily be the same. Figures 3 and 4 show the thermograms for the amylose and amylopectin of potato and wheat starches, respectively. In both cases the thermograms of amylose and amylopectin are quite distinct, the temperatures of the initial endotherms being lower for amylopectin (295 °C) than for amylose (303

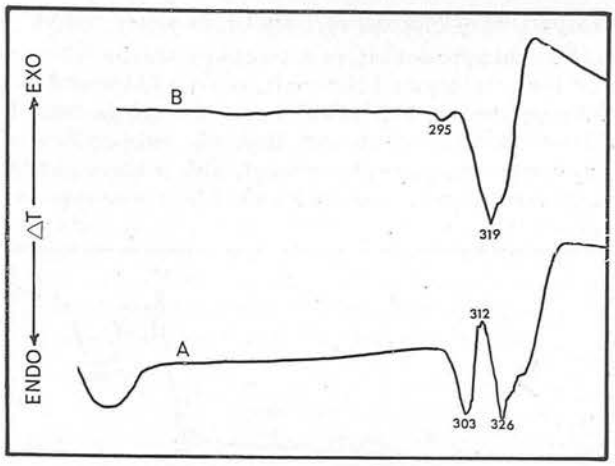

Fig. 3. Thermograms of (A) potato amylose, and (B) potato amylopectin (Temperatures in °C).

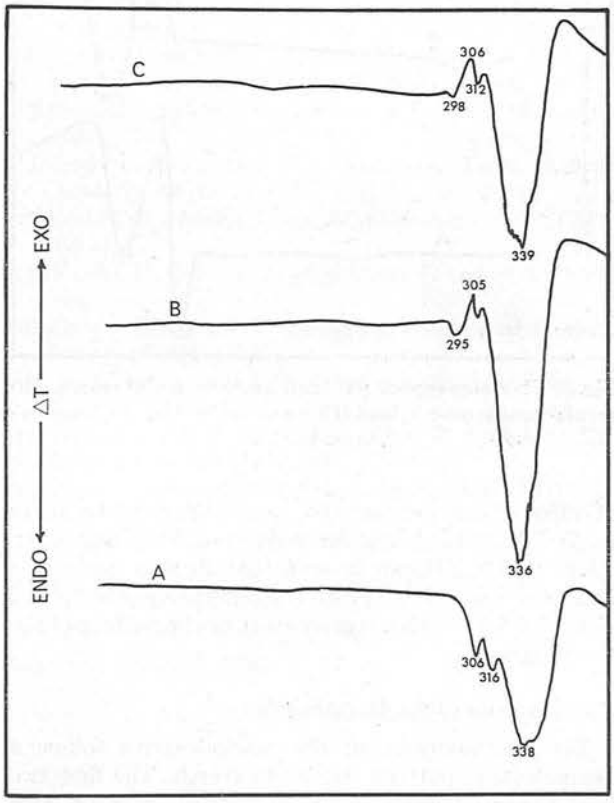

Fig. 4. Thermograms of (A) wheat amylose, (B) wheat amylopectin, and (C) non-granular wheat starch (Temperatures in °C).

and 306 °C). It is of interest to note that, in both cases, the temperature of the initial endotherm of the starch is lower than that of either of its components (compare Fig. 2). However, when the granular structure was destroyed by dissolving the starch in dimethyl sulphoxide and precipitating the now non-granular starch with ethanol, the expected result for a starch consisting of 75 % amylopectin and 25 % amylose is obtained, as shown in Figure 4. The pattern of the thermogram and the temperature of the initial endotherm become intermediate to those of amylose and amylopectin, and bear a closer resemblance to those of amylopectin.

Comparison of Starches of Varying Amylose Content

It would appear that, in determining the initial reaction temperature and the characteristic pattern of the thermograms, the physical structure of the starch granule is more important than the proportions of amylose and amylopectin present. This is borne out by the thermograms shown in Figure 5 for maize starches

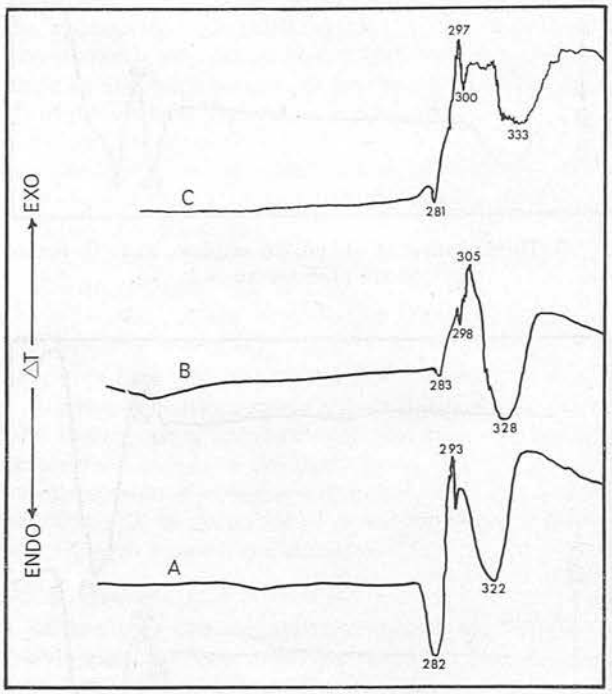

Fig. 5. Thermograms of (A) high amylose maize starch, (B) regular maize starch, and (C) waxy maize starch (Temperatures in °C).

of different amylose content, i.e. a high-amylose maize (~ 70 % amylose), regular maize (~ 28 %) and waxy maize (< 1 %). It can be seen that there is apparently little correlation between the amylose-content, and either initial reaction temperature or the pattern of the thermogram.

Thermograms of the Maltodextrins

The thermograms of the maltodextrins follow a characteristic pattern similar to starch. The first two in the series, glucose and maltose, are somewhat anomalous, as might be expected. Thermograms for G_1, G_2 and G_3 are shown in Figure 6. In each case, a very small endotherm was followed by a large exotherm when decomposition began. For the higher oligomers exactly comparable thermograms were obtained except that the thermal stability of these oligosaccharides increases with increasing chainlength. This is demonstrated in Table 2 in which the temperatures of the large exotherms at the beginning of decomposition are given.

Table 2

Characteristic Exotherms for Maltodextrins

Oligomer.	G_1	G_2	G_3	G_4	G_5	G_6	G_7
Exotherm (°C)	185	145	166	180	188	207	220

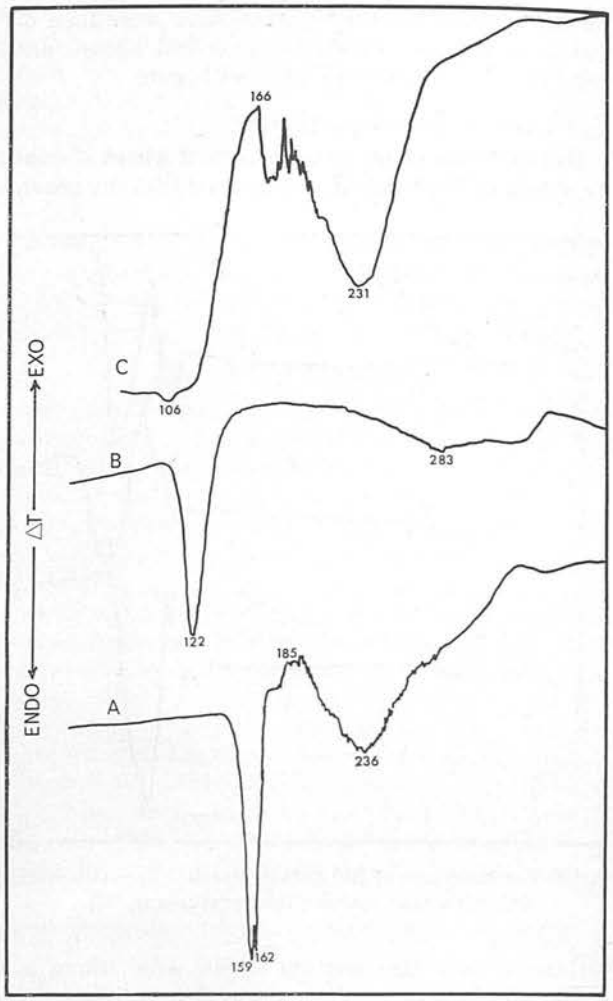

Fig. 6. Thermograms of (A) G_1, (B) G_2 and (C) G_3 (Temperatures in °C).

Acknowledgement

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Summary

A study of the thermal degradation of maltodextrins and of starch and its components has been made using differential thermal analysis (DTA). It was found that:

1. the presence of alumina and sodium chloride profoundly affected the thermogram of starch. DTA should, therefore, preferably be carried out in the absence of salt.
2. the differences in the thermograms of common starches from different botanical sources were not large enough for the different starches to be characterized by DTA.
3. the initial reaction temperature for amylopectin was lower than that of amylose.
4. the physical structure of the starch granule was of more importance than the proportions of amylose and amylopectin in determining the initial reaction temperature and pattern of the thermogram of a starch.
5. the thermograms of the maltodextrins are similar to those of starch, the thermal stability of the oligomers increasing with chainlength.

Über den Wärmeabbau von Stärke VII. Differential-Thermoanalyse von Maltodextrinen und von Stärke und Stärkekomponenten

Zusammenfassung

Unter Zuhilfenahme der Differential-Thermoanalyse (DTA) wurde der Wärmeabbau von Maltodextrinen, von Stärke und Stärkekomponenten untersucht. Dabei ergab sich folgendes:

1. *Die Anwesenheit von Aluminiumoxid und Natriumchlorid wirkte sich sehr stark auf das Stärke-Thermogramm aus. Bei einer DTA sollte daher nach Möglichkeit kein Salz anwesend sein.*
2. *Die Unterschiede in den Thermogrammen gewöhnlicher Stärken verschiedener botanischer Herkunft waren nicht so groß, daß man eine DTA zur Unterscheidung solcher Stärken heranziehen könnte.*
3. *Die Anfangs-Reaktionstemperatur lag bei Amylopektin niedriger als bei Amylose.*
4. *Die physikalische Struktur des Stärkekorns war für die Anfangs-Reaktionstemperatur und die Art des Stärke-Thermogramms von größerer Bedeutung als das Verhältnis zwischen Amylose und Amylopektin.*
5. *Die Thermogramme der Maltodextrine ähneln den Stärke-Thermogrammen, wobei die Wärmestabilität der Oligomere mit der Kettenlänge zunimmt.*

La Dégradation thermique de l'Amidon VII. Analyse thermique différentielle de Maltodextrines et d'Amidon et de ses Composantes

Resumé

On a étudié la dégradation thermique de maltodextrines ainsi que d'amidon et de ses composantes à l'aide d'une analyse thermique différentielle (ATD), et a trouvé les faits suivants:

1. *La présence de l'oxyde d'aluminium et du chlorure de sodium, a fortement influencé le thermogramme de l'amidon. Si possible, une ATD devrait donc s'effectuer en l'absence de sel.*
2. *Les différences dans les thermogrammes d'amidons ordinaires de provenances botaniques différentes n'étaient pas suffisamment grandes pour permettre une discrimination de ces amidons différents à l'aide d'une ATD.*
3. *La température de réaction initiale de l'amylopectine était plus basse que celle de l'amylose.*
4. *La structure physique du grain d'amidon était plus importante en déterminant la température de réaction initiale et la nature du thermogramme de l'amidon que la proportion entre l'amylose et l'amylopectine.*
5. *Les thermogrammes des maltodextrines ressemblent ceux de l'amidon, et la stabilité à la chaleur des oligomères y accroît avec la longueur des chaînes.*

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